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(54) **ADSORBENT MATERIALS AND METHODS OF ADSORBING CARBON DIOXIDE**

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See application file for complete search history.

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(57) **ABSTRACT**

Methods of designing zeolite materials for adsorption of CO_2. Zeolite materials and processes for CO_2 adsorption using zeolite materials.

12 Claims, 6 Drawing Sheets

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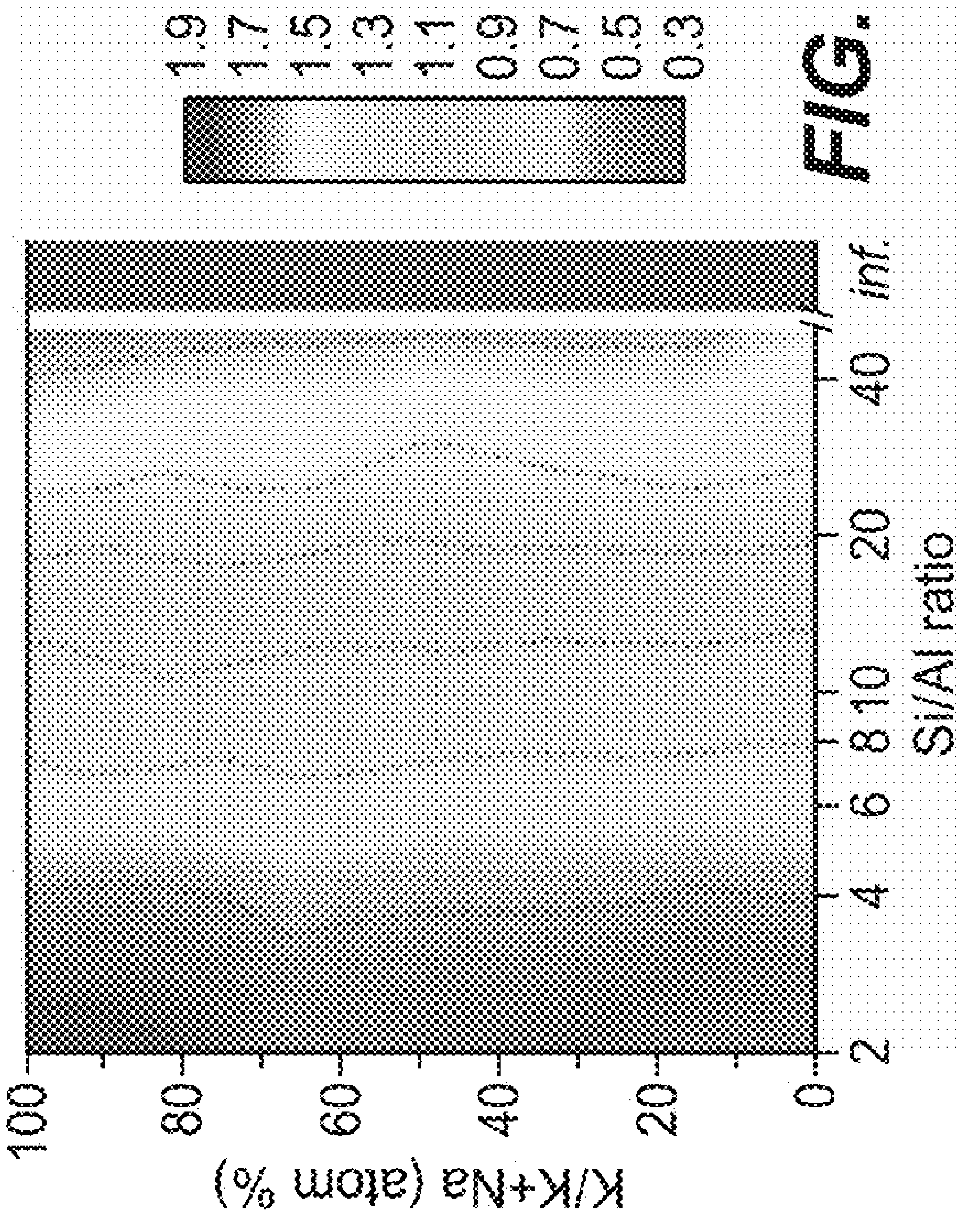

FIG. 1A

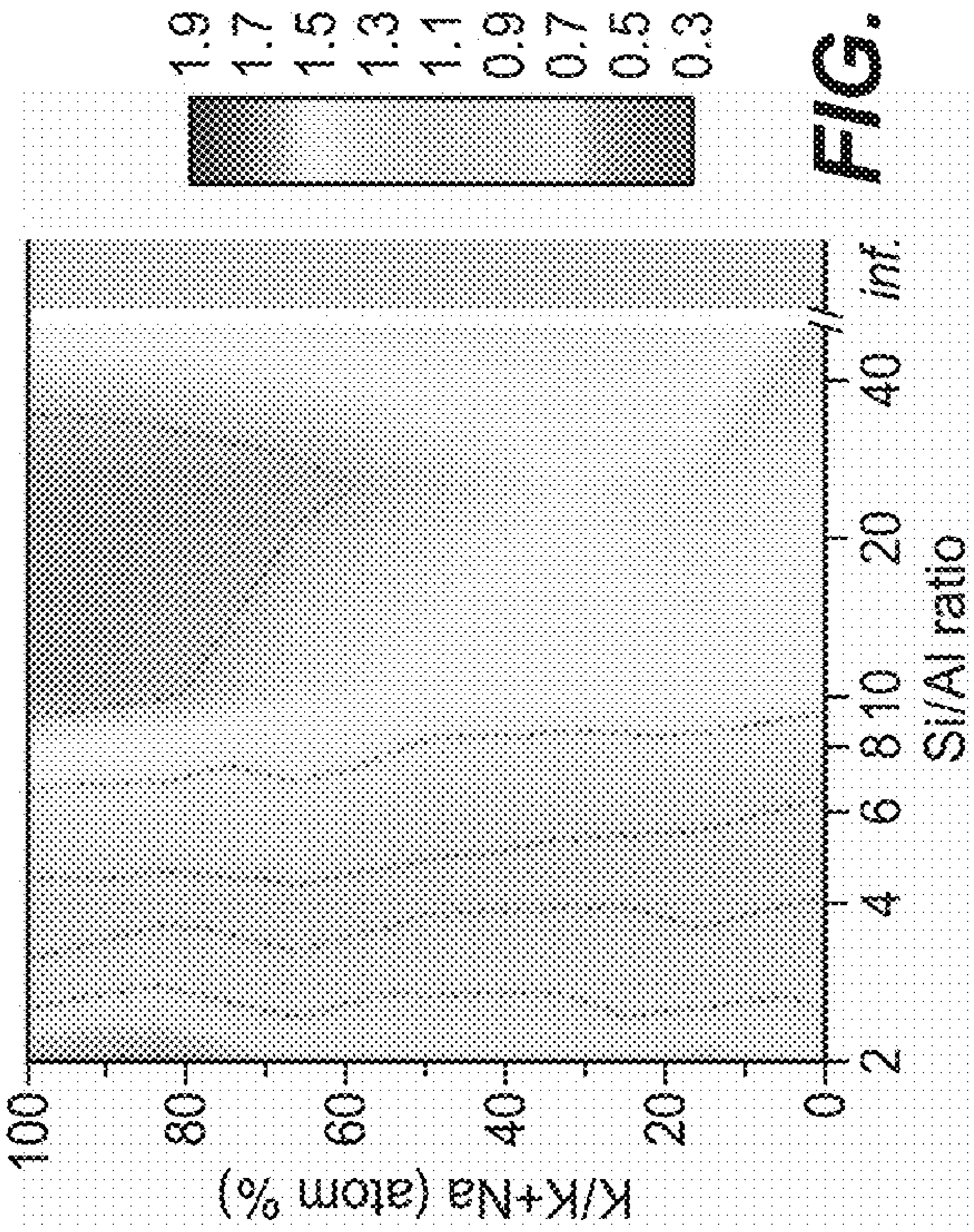

FIG. 1B

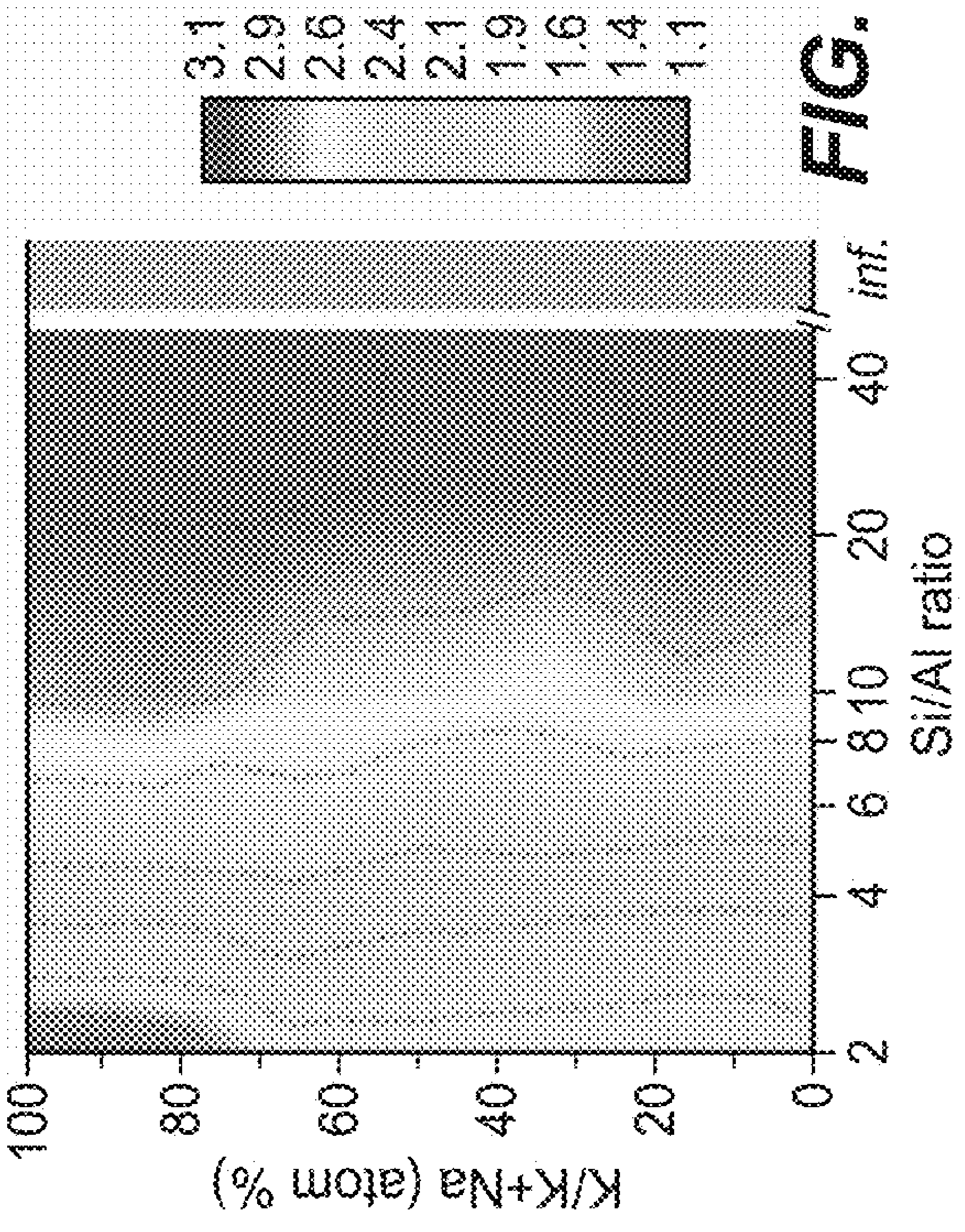

FIG. 1C

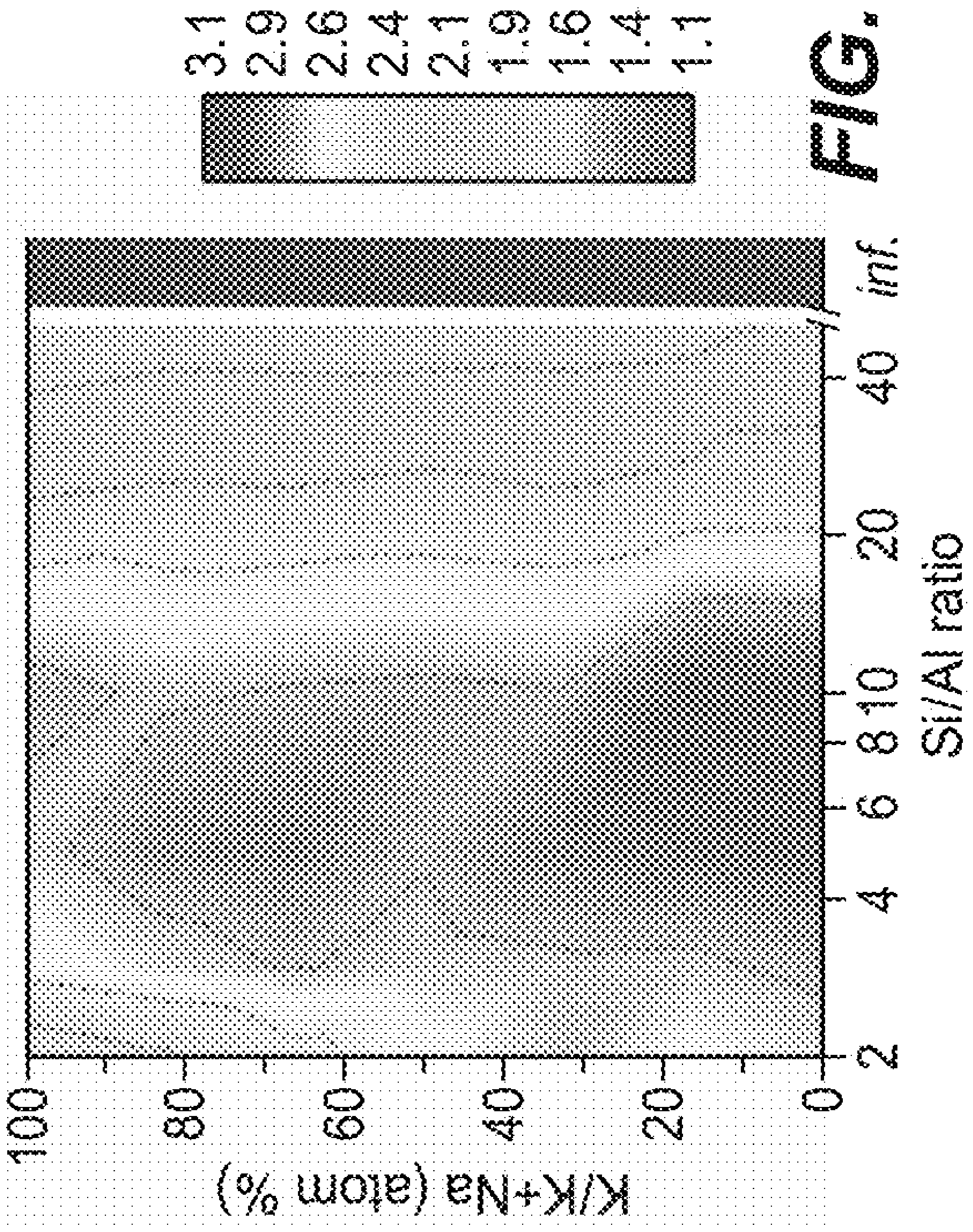

FIG. 1D

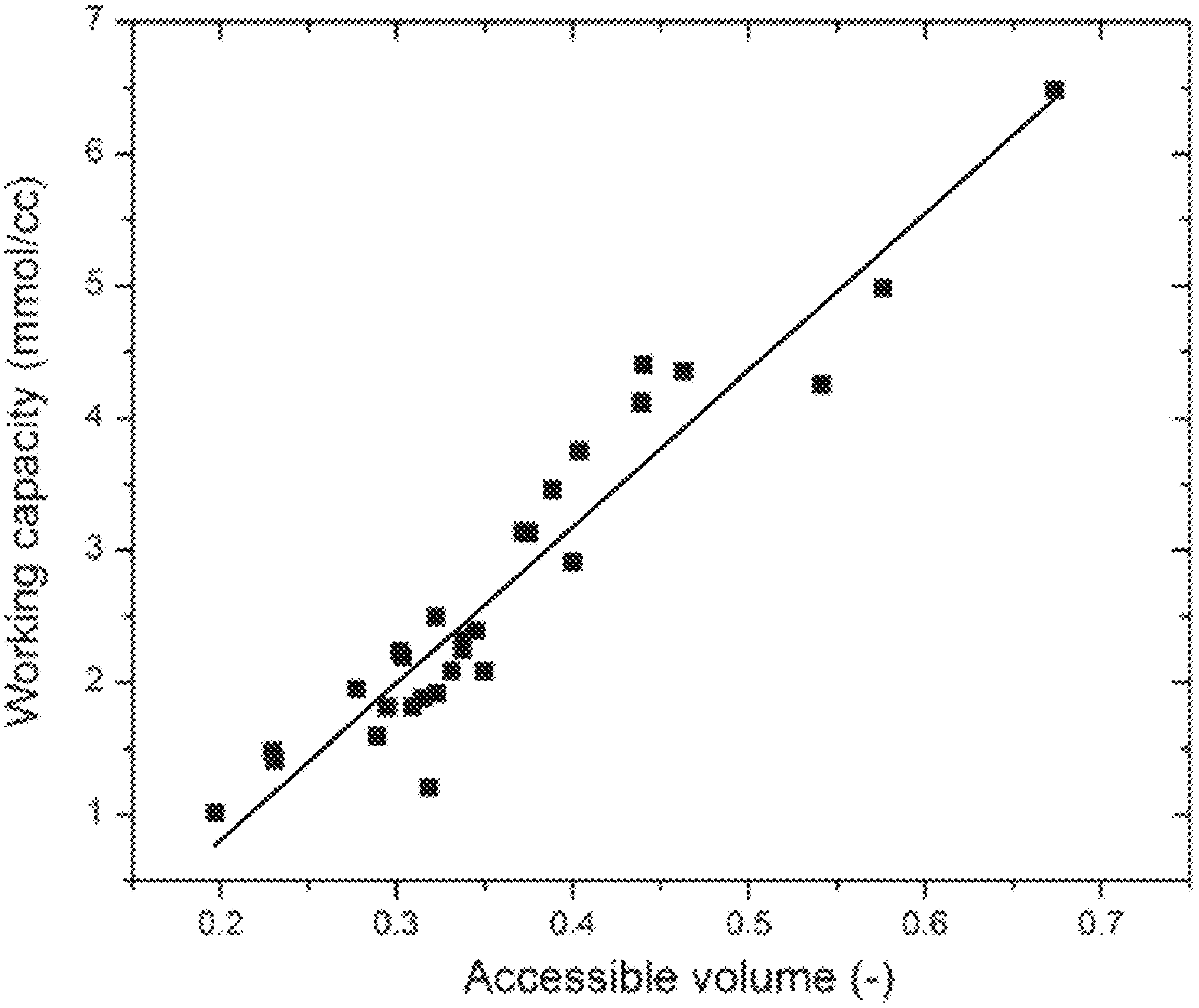
Working capacity (mmol/cc)
1
2
3
4
5
6
7
0.2
0.3
0.4
0.5
0.6
0.7
Accessible volume (-)

FIG. 2

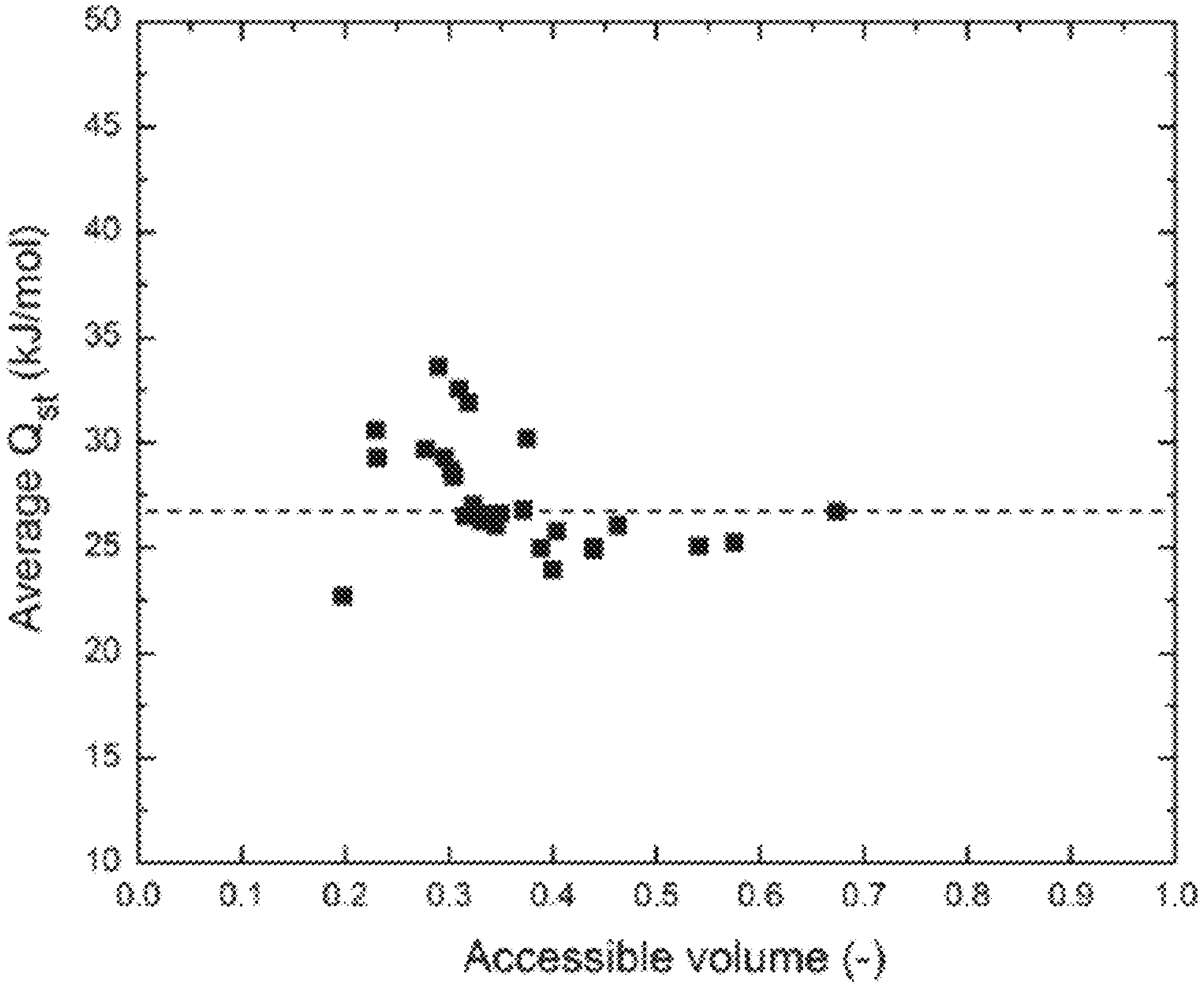
Average Q_{st} (kJ/mol)
10
15
20
25
30
35
40
45
50
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Accessible volume (-)

FIG. 3

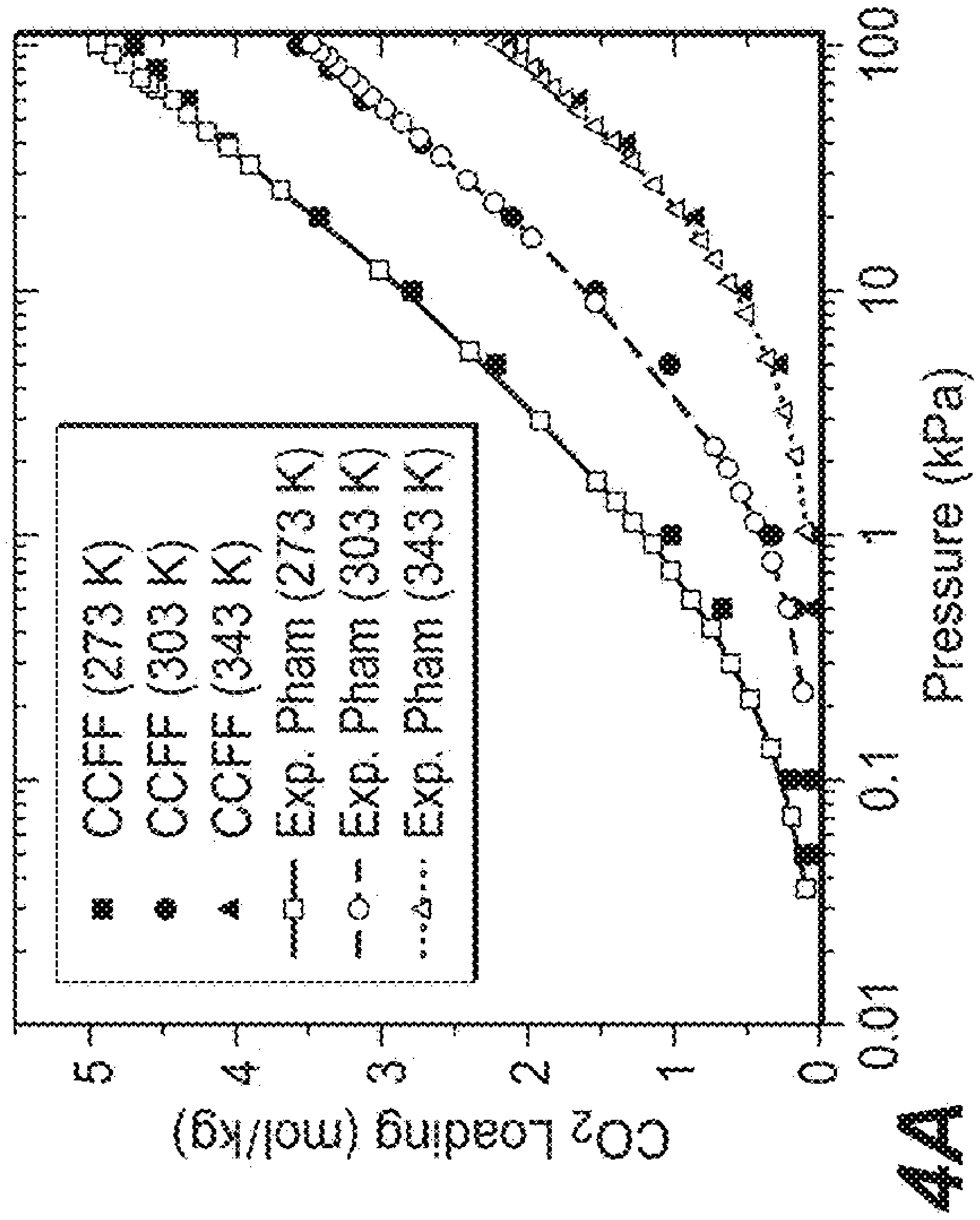

FIG. 4A

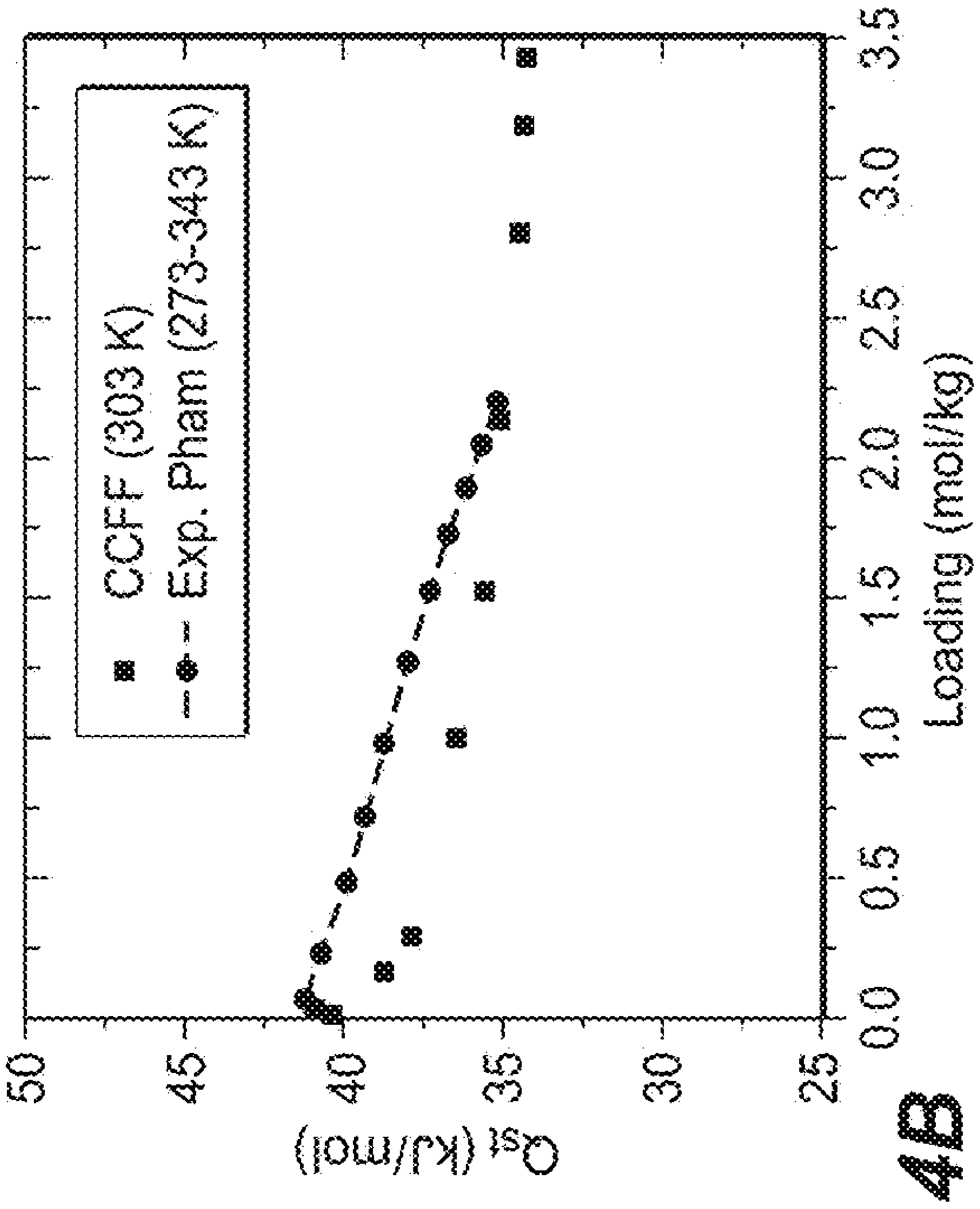

FIG. 4B

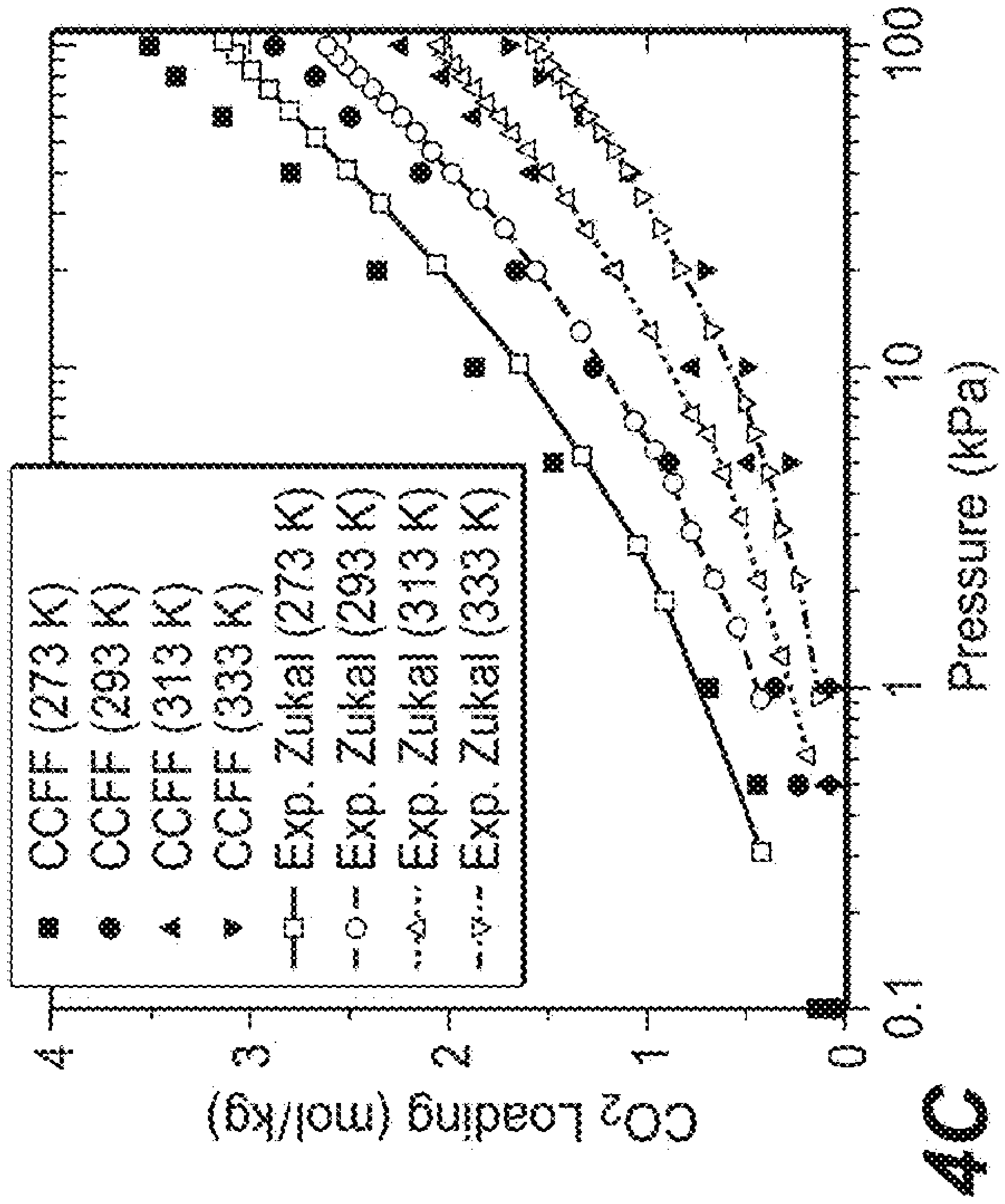

FIG. 4C

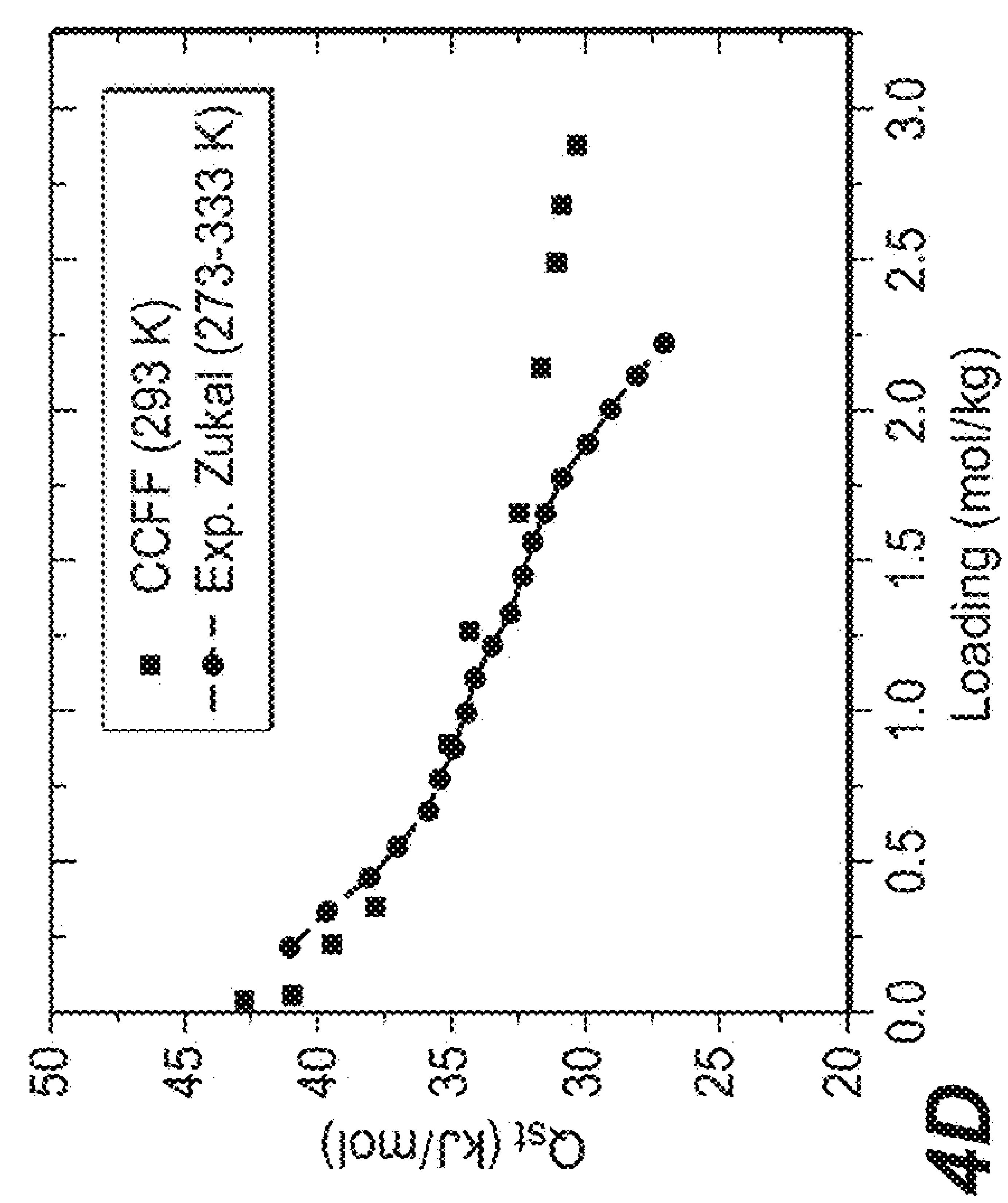

FIG. 4D

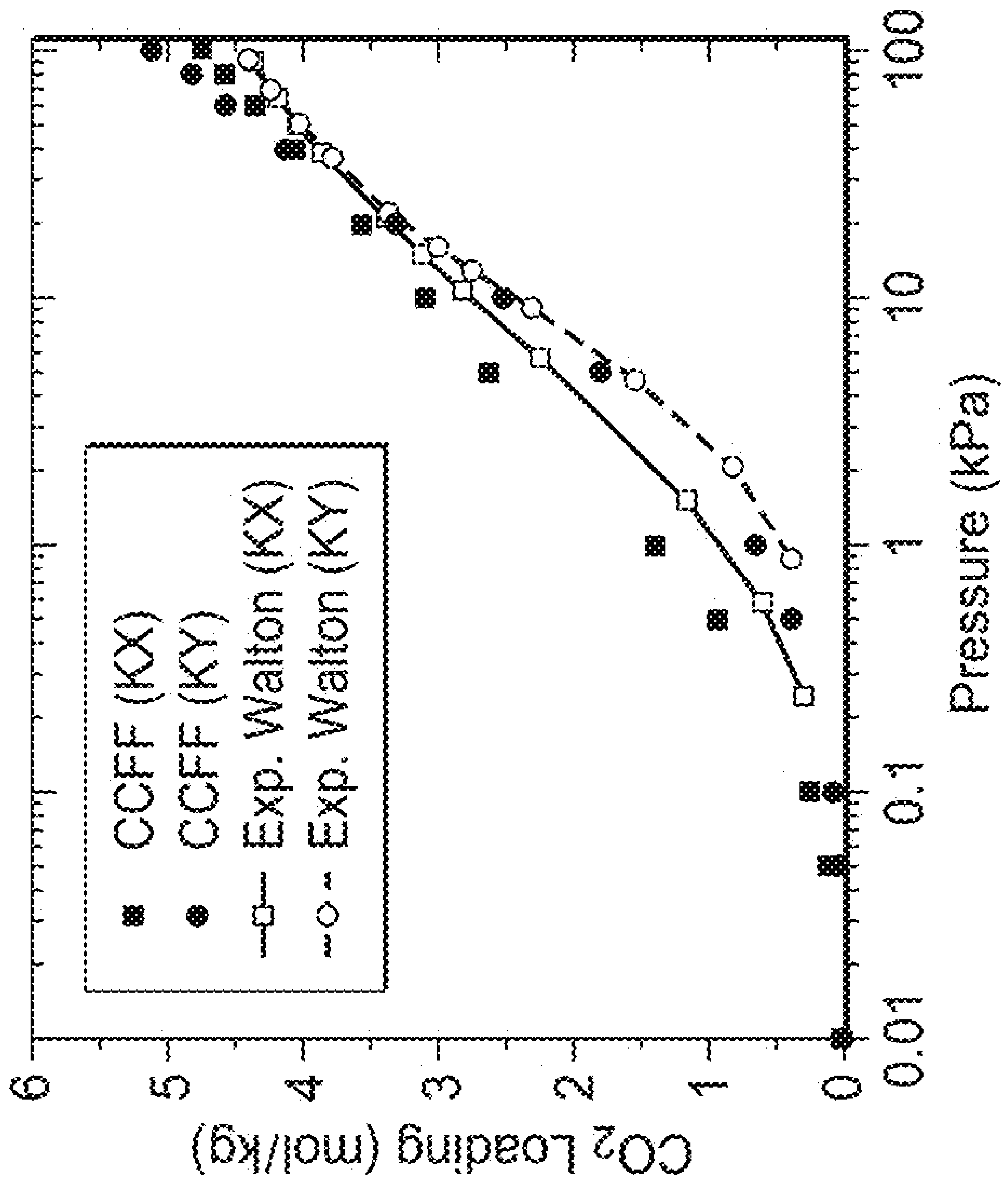
CO2 Loading (mol/kg)
0
1
2
3
4
5
6
Pressure (kPa)
0.01
0.1
1
10
100
CCFF (KX)
CCFF (KY)
Exp. Walton (KX)
Exp. Walton (KY)

FIG. 4E

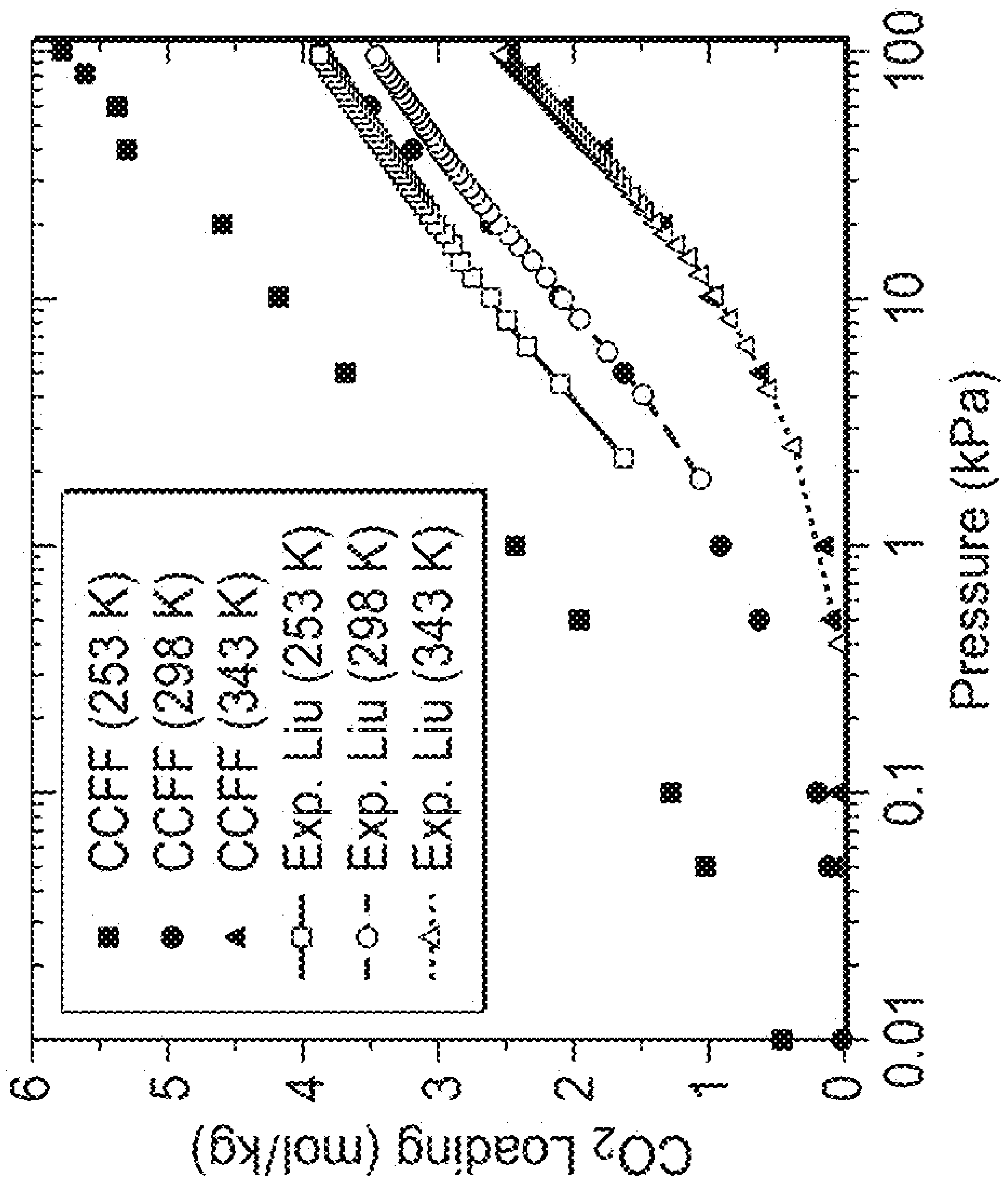
CO2 Loading (mol/kg)
0
1
2
3
4
5
6
Pressure (kPa)
0.01
0.1
1
10
100
CCFF (253 K)
CCFF (298 K)
CCFF (343 K)
Exp. Liu (253 K)
Exp. Liu (298 K)
Exp. Liu (343 K)

FIG. 4F

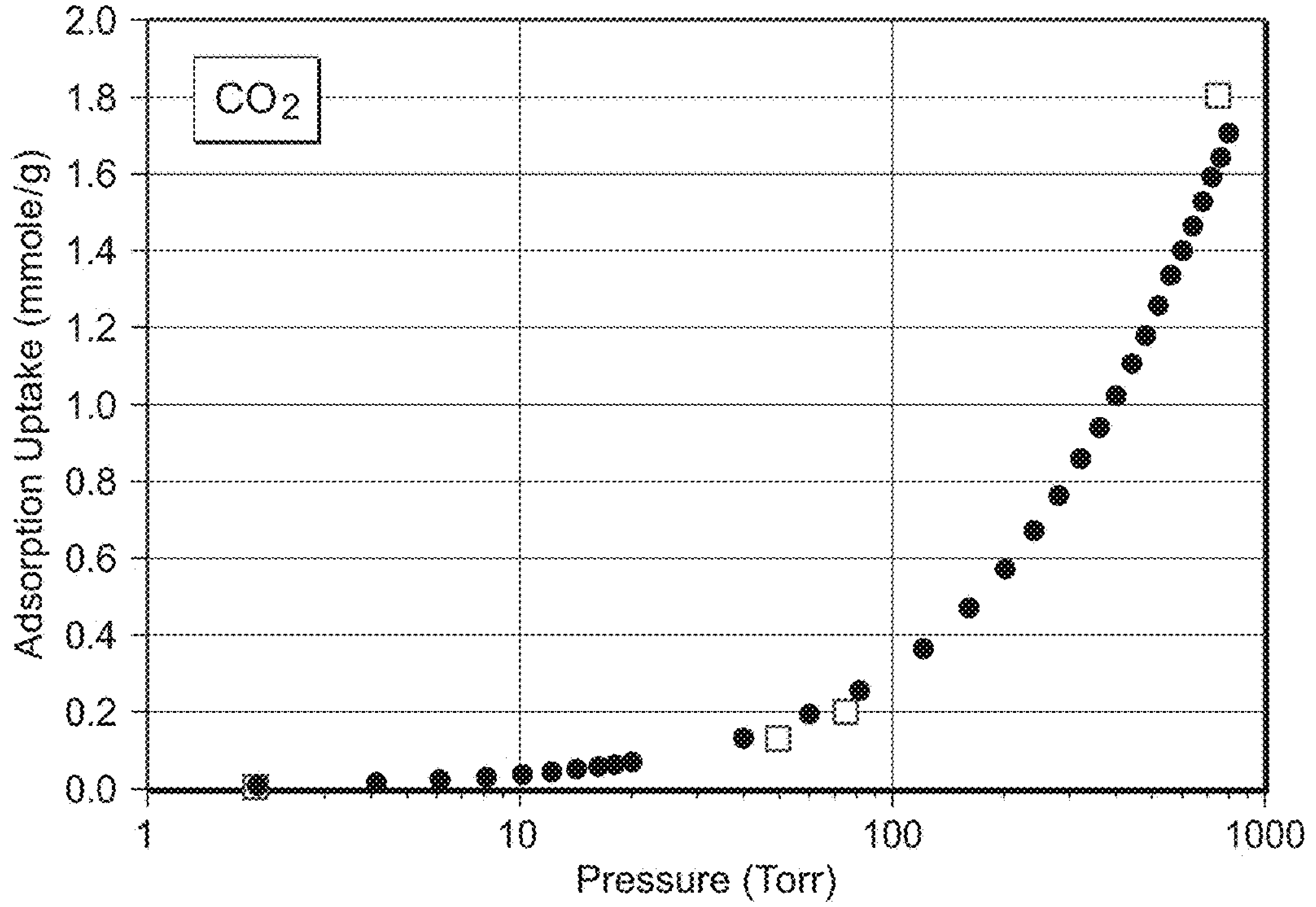
CO$_2$
Adsorption Uptake (mmole/g)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1
10
100
1000
Pressure (Torr)

FIG. 5

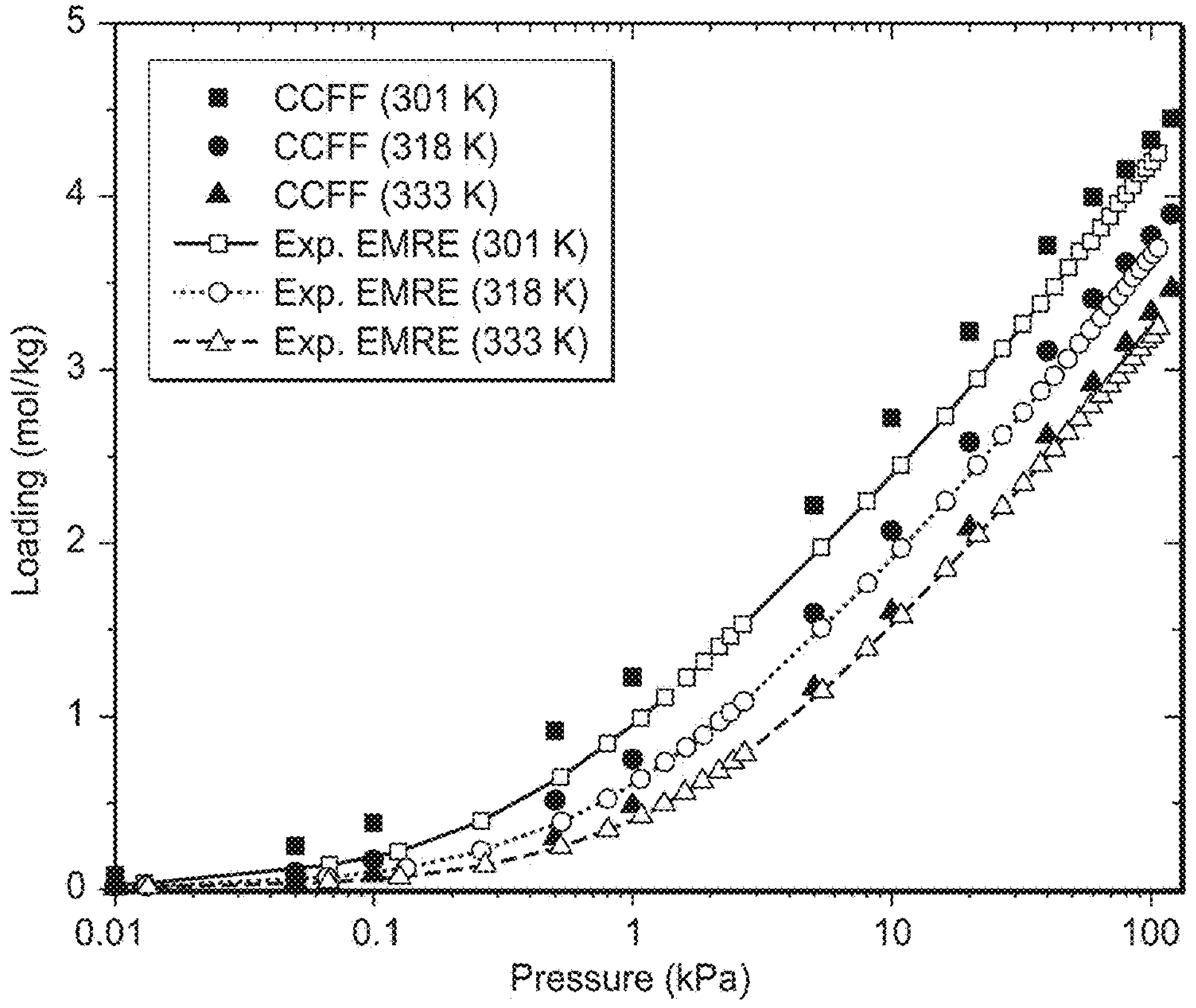
CCFF (301 K)
CCFF (318 K)
CCFF (333 K)
Exp. EMRE (301 K)
Exp. EMRE (318 K)
Exp. EMRE (333 K)
Loading (mol/kg)
5
4
3
2
1
0
0.01
0.1
1
10
100
Pressure (kPa)

FIG. 6

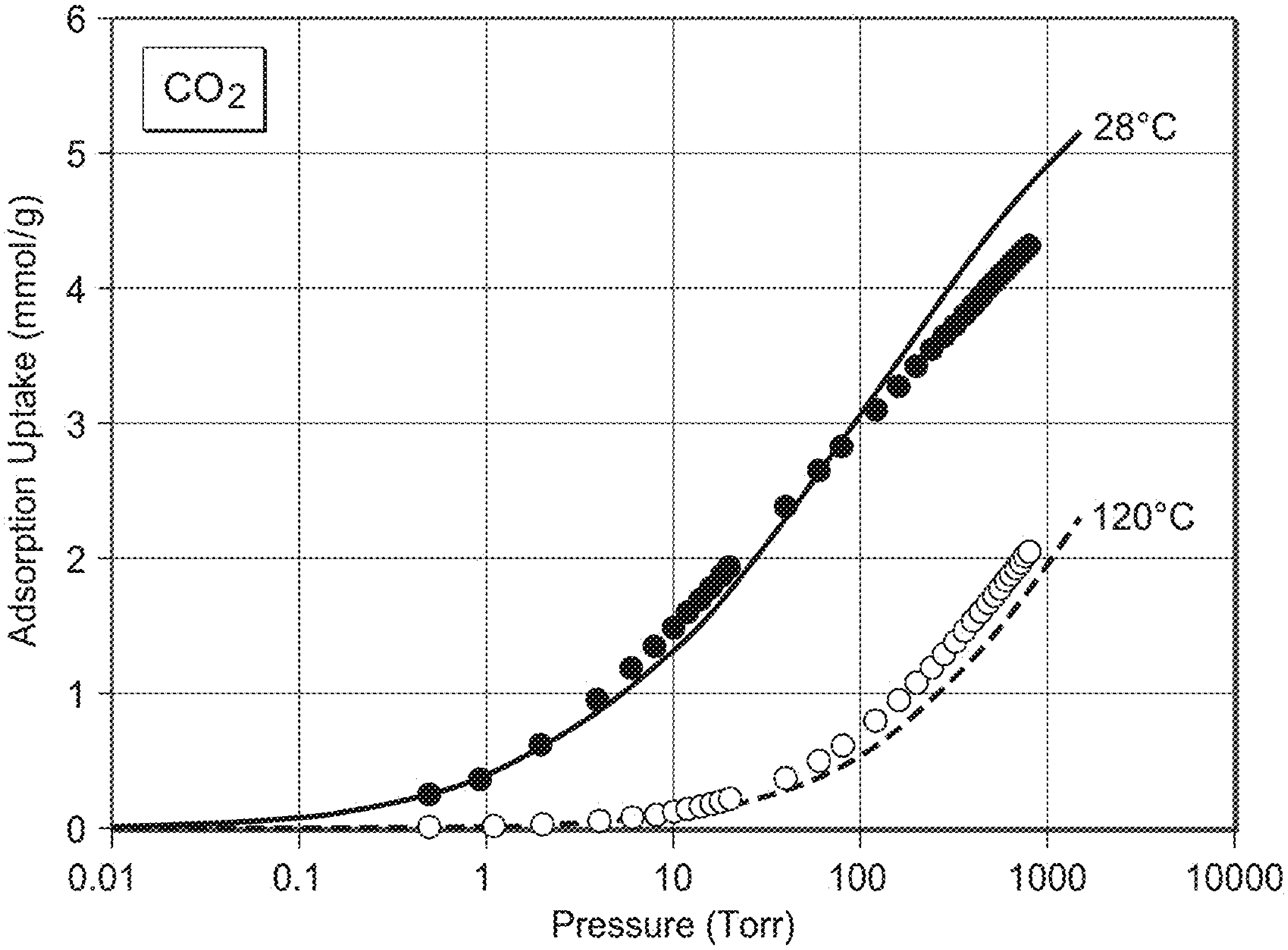
CO$_2$
28°C
120°C
Adsorption Uptake (mmol/g)
0
1
2
3
4
5
6
0.01
0.1
1
10
100
1000
10000
Pressure (Torr)

FIG. 7

ADSORBENT MATERIALS AND METHODS OF ADSORBING CARBON DIOXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application No. 62/337,991, filed 18 May 2016, entitled Absorbent Materials And Methods Of Absorbing Carbon Dioxide and U.S. Provisional Patent Application No. 62/255,789, filed 16 Nov. 2015, entitled Absorbent Materials And Methods Of Absorbing Carbon Dioxide, the entirety of which is incorporated by reference herein.

FIELD

The present invention relates to methods of designing zeolite materials for adsorption of CO_2 and processes for CO_2 adsorption.

BACKGROUND

Gas separation is important in many industries for removing undesirable contaminants from a gas stream and for achieving a desired gas composition. For example, natural gas from many gas fields can contain significant levels of H_2O, SO_2, H_2S, CO_2, N_2, mercaptans, and/or heavy hydrocarbons that have to be removed to various degrees before the gas can be transported to market. It is preferred that as much of the acid gases H_2S and CO_2 be removed from natural gas as possible to leave methane as the recovered component. Natural gas containing a high concentration of CO_2 should not be directly introduced into pipelines because it may be corrosive to the pipelines in the presence of water. Furthermore, small increases in recovery of methane can result in significant improvements in process economics and also serve to prevent unwanted resource loss. It is desirable to recover more than 80 vol %, particularly more than 90 vol %, of the methane when detrimental impurities are removed.

Additionally, synthesis gas (syngas) typically requires removal and separation of various components before it can be used in fuel, chemical and power applications because all of these applications have a specification of the exact composition of the syngas required for the process. As produced, syngas can contain at least CO and H_2. Other molecular components in syngas can be CH_4, CO_2, H_2S, H_2O, N_2, and combinations thereof. Minority (or trace) components in the gas can include hydrocarbons, NH_3, NO_x, and the like, and combinations thereof. In almost all applications, most of the H_2S should typically be removed from the syngas before it can be used, and, in many applications, it can be desirable to remove much of the CO_2.

Adsorptive gas separation techniques are common in various industries using solid sorbent materials such as activated charcoal or a porous solid oxide such as alumina, silica-alumina, silica, or a crystalline zeolite. The selection of suitable zeolite materials is critical for CO_2 capture and separation. However, a significant challenge exists in arriving at suitable materials because of the large diversity of zeolite compositions. For example, there are approximately 220 zeolite topologies recognized by the International Zeolite Society, which may have varying Si/Al ratios as well as varying cation concentrations resulting in numerous possible zeolite materials. Thus, there is not only a need for zeolite materials with improved adsorption capacity for a gas contaminant, such as CO_2, which can be used in various gas separation processes but also a need for improved methods for identifying suitable zeolite materials for CO_2 adsorption.

SUMMARY

Thus, in one aspect, embodiments of the invention provide a pressure swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, DAC, EMT, EUO, IMF, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of CAS, EMT, FAU, HEU, IRR, IRY, ITT, LTA, RWY, TSC and VFI, and a combination thereof, having: (a) a Si/Al ratio of about 5 to about 85; and (b) a potassium cation concentration of about 5% to about 100%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) reducing the pressure in the adsorption bed to a second pressure resulting in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

In still another aspect, embodiments of the invention provide a pressure swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite having a Si/Al ratio of between about 5 and about 45 and with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) reducing the pressure in the adsorption bed to a second pressure resulting in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

In still another aspect, embodiments of the invention provide an a pressure temperature swing adsorption process for separating a CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof; or a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, EMT, EUO, FAU, IRR, IRY, ITT, KFI, LTA, MRE, MWW, NES, PAU, RHO, RWY, SFF, STI, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 3 to about 100; and (b) a potassium cation concentration of about 1% to about 100%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating the adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a first portion of CO_2; and d) reducing the pressure of the adsorbent bed to a second pressure lower than the first pressure and recovering a second portion of CO_2.

In still another aspect, embodiments of the invention provide a vacuum swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following; (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of CAS, DAC, HEU, LAU, MTT, RRO, TON, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, EMT, EUO, IMF, IRR, IRY, ITH, ITT, KFI, MFS, MRE, MWW, NES, PAU, RWY, SFF, STF, STI, SZR, TER, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100; and (b) a potassium cation concentration of about 0% to about 100%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure and in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

In still another aspect, embodiments of the invention provide a vacuum swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI and a combination thereof, having (a) a Si/Al ratio of about 3 to about 30; and (b) a potassium cation concentration of about 40% to about 100%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure and in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

In still another aspect, embodiments of the invention provide a vacuum temperature swing adsorption process for separating a CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 with a CAS framework structure; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, EMT, EUO, HEU, IMF, IRR, IRY, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100; and (b) a potassium cation concentration of about 0% to about 100%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) simultaneously heating the adsorbent bed to a second temperature higher than the first temperature and passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2.

In still another aspect, embodiments of the invention provide a vacuum temperature swing adsorption process for separating a CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, MFI, RHO, UFI and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 5% to about 40%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; and c) simultaneously heating the adsorbent bed to a second temperature higher than the first temperature and passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2.

In still another aspect, embodiments of the invention provide a temperature swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of AFT AFX, CAS, EMT, IRR, IRY, ITT, KFI, MWW, PAU, RWY, SFF, STF, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 0% to about 50%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2 from the adsorbent bed.

In still another aspect, embodiments of the invention provide a temperature swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, RHO, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 5% to about 40%; wherein the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2 from the adsorbent bed.

Other embodiments, including particular aspects of the embodiments summarized above, will be evident from the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1***a*-**1***d* illustrate contour plots of CO_2 working capacity (mol/kg) as a function of Si/Al ratio and K/(K+Na) % (potassium cation concentration) for MWW structures in (a) PSA1, (b) VSA, (c) PTSA1, and (d) VTSA1 processes.

FIG. **2** illustrates a relationship between the working capacity and the accessible pore volume of adsorbents for a pressure swing adsorption (PSA) process.

FIG. **3** illustrates average heats of adsorption (Q_{st}) at adsorption and desorption conditions for the optimal composition of each topology for the PSA process. The dashed line indicates the mean value of the average Q_{st} for all optimal compositions.

FIGS. **4**(*a*)-(*f*) illustrate comparison of simulated and experimental adsorption properties of CO_2 in K-exchanged and K/Na-exchanged zeolites as follows: (a) isotherms and (b) isosteric heats of adsorption in K-CHA (Si/Al=12), (c) isotherms and (d) isosteric heats of adsorption in K-MCM-22 (Si/Al=15), (e) isotherms in KX (Si/Al=1.23) and KY (Si/Al=2.37) at 298 K, and (f) isotherms in K/Na-LTA (Si/Al=1, 17.4% K). The experimental data are from Pham et al. (Pham, T. D.; Liu, Q. L.; Lobo, R. F. *Langmuir* 2013, 29, 832), Zukal et al. (Zukal, A.; Pawlesa, J.; Cejke, J. *Adsorption* 2009, 15, 264), Walton et al. (Walton, K. S.; Abney, M. B.; LeVan, M. D. *Micropor Mesopor Mat* 2006, 91, 78), and Liu et al. (Liu, Q. L.; Mace, A.; Bacsik, Z.; Sun, J. L.; Laaksonen, A.; Hedin, N. *Chem Commun* 2010, 46, 4502). Lines are drawn to guide the eye.

FIG. **5** illustrates a CO_2 adsorption isotherm for SSZ-35 (circles) compared to the simulated CO_2 adsorption (open squares).

FIG. **6** illustrates CO_2 adsorption isotherms at different temperatures (open symbols) for SSZ-13 (circles) compared to the simulated CO_2 adsorption isotherms (points).

FIG. **7** illustrates a CO_2 adsorption isotherm for SSZ-16 (points) compared to the simulated CO_2 adsorption (lines) at 28° C. and 120° C.

DETAILED DESCRIPTION

In various aspects of the invention, adsorbent materials, adsorbent contactors and gas separation processes using the adsorbent materials are provided.

I. Definitions

To facilitate an understanding of the present invention, a number of terms and phrases are defined below.

As used in the present disclosure and claims, the singular forms "a," "an," and "the" include plural forms unless the context clearly dictates otherwise.

Wherever embodiments are described herein with the language "comprising," otherwise analogous embodiments described in terms of "consisting of" and/or "consisting essentially of" are also provided.

The term "and/or" as used in a phrase such as "A and/or B" herein is intended to include "A and B", "A or B", "A", and "B".

As used herein, the term "adsorption" includes physisorption, chemisorption, and condensation onto a solid support, adsorption onto a solid supported liquid, chemisorption onto a solid supported liquid and combinations thereof.

As used herein, the term "breakthrough" refers to the point where the product gas leaving the adsorbent bed exceeds the target specification of the contaminant component. At the breakthrough point, the adsorbent bed can be considered "spent", such that any significant further operation through the spent adsorption bed alone will result in off-specification product gas. As used herein, the "breakthrough" can generally coincide with the "adsorption front", i.e., at the time breakthrough is detected at the outlet of the adsorbent bed, the adsorption front is generally located at the end of the adsorption bed.

As used herein, the term "selectivity" refers to a binary (pairwise) comparison of the molar concentration of components in the feed stream and the total number of moles of these components adsorbed by the particular adsorbent during the adsorption step of the process cycle under the specific system operating conditions and feedstream composition. For a feed containing component A, component B, as well as additional components, an adsorbent that has a greater "selectivity" for component A than component B will have at the end of the adsorption step of the swing adsorption process cycle a ratio:

$$U_A = (\text{total moles of } A \text{ in the adsorbent})/(\text{molar concentration of } A \text{ in the feed})$$

that is greater than the ratio:

$$U_B = (\text{total moles of } B \text{ in the adsorbent})/(\text{molar concentration of } B \text{ in the feed})$$

Where U_A is the "Adsorption Uptake of component A" and U_B is the "Adsorption Uptake of component B".

Therefore for an adsorbent having a selectivity for component A over component B that is greater than one:

$$\text{Selectivity} = U_A/U_B \text{ (where } U_A > U_B\text{)}.$$

As used herein, the term "kinetic selectivity" refers to the ratio of single component diffusion coefficients, D (in m^2/sec), for two different species. These single component diffusion coefficients are also known as the Stefan-Maxwell transport diffusion coefficients that are measured for a given adsorbent for a given pure gas component. Therefore, for example, the kinetic selectivity for a particular adsorbent for component A with respect to component B would be equal to D_A/D_B. The single component diffusion coefficients for a material can be determined by tests well known in the adsorptive materials art. The preferred way to measure the kinetic diffusion coefficient is with a frequency response technique described by Reyes et al. in "Frequency Modulation Methods for Diffusion and Adsorption Measurements in Porous Solids", J. Phys. Chem. B. 101, pages 614-622, 1997. In a kinetically controlled separation it is preferred that kinetic selectivity (i.e., D_A/D_B) of the selected adsorbent for the first component (e.g., Component A) with respect to the second component (e.g., Component B) be greater than 5, greater than 20, and particularly greater than 50.

As used herein, the term "equilibrium selectivity" is defined in terms of the slope of the single component uptake into the adsorbent (in μmole/g) vs. pressure (in torr) in the linear portion, or "Henry's regime", of the uptake isotherm for a given adsorbent for a given pure component. The slope of this line is called herein the Henrys constant or "equilibrium uptake slope", or "H". The "equilibrium selectivity" is defined in terms of a binary (or pairwise) comparison of the Henrys constants of different components in the feed for a particular adsorbent. Therefore, for example, the equilibrium selectivity for a particular adsorbent for component A with respect to component B would be HA/HB. It is preferred that in an equilibrium controlled separation the equilibrium selectivity (i.e., HA/HB) of the selected adsorbent for the first component (e.g., Component A) with respect to the second component (e.g., Component B) be greater than 5, greater than 20, and particularly greater than 50.

As used herein, the term "Si/Al ratio" is defined as the molar ratio of silica to alumina of a zeolitic structure.

II. Methods of Designing Zeolite Materials for CO_2 Adsorption

In a first embodiment, a method of designing a zeolite material for CO_2 adsorption is provided. To describe adsorption of CO_2 molecules in zeolites, the following three interactions need to be studied: 1) CO_2-zeolite; 2) cation-framework structure; and 3) CO_2—CO_2. The EPM2 model (see Harris and Young, *J. Phys. Chem.*, 1995, 99 12021) may be used to represent the CO_2—CO_2 interaction because the phase behavior of pure CO_2 is correctly captured. For the CO_2-zeolite and the cation-framework structure interactions, a first-principles-based force fields for crystalline porous materials approach may be used. Specifically, a fully periodic framework to represent adsorbent structure may be used and quantum chemistry calculations for numerous adsorption configurations randomly scattered throughout the whole framework may be made. This approach may be used for adsorption of CO_2 in siliceous zeolites and also for cation exchanged zeolites (e.g., potassium cation, sodium cation, etc.). See Fang et al., *J. Phys. Chem. C,* 2012, 116, 10692; Fang et al., *Phys Chem. Chem. Phys.,* 2013, 15, 12882. The developed force fields may accurately predict experimental adsorption properties and show transferability across different zeolite topologies. An example of first-principles-derived force field parameters are shown in Tables 1, 2 and 3 below.

TABLE 1

First-Principles-Derived Force Field Parameters For CO_2 In K/Na-Exchanged Zeolites--Shown Are Lennard-Jones Potential Parameters And Partial Charges For Coulombic Interactions

	CCFF		
Cross Species	ε/k_b (K)	σ (Å)	Charge (e)
Si—C	49.75	3.620	Si (2.21)
Si—O	38.90	3.494	O_z^{Si} (−1.105)
O_z—C	29.12	3.193	O_z^{Al} (−1.32)
O_z—O	23.43	3.067	Al (2.08)
Al—C	32.21	3.366	K (0.99)
Al—O	25.32	3.246	Na (0.99)
K—C	60.60	3.232	H (0.51)
K—O	48.19	3.111	
Na—C	66.78	2.827	
Na—O	54.76	2.707	
H—O	225.46	1.969	
H—C	270.70	2.061	

TABLE 2

Buckingham Parameters For K- And Na-Framework Interactions

Cross Species	A (eV)	B (Å)	C (eV)
K—O_z	5258.3	0.2916	193.7
Na—O_z	3261.6	0.2597	45.4

TABLE 3

Morse Potential Parameters For H-Framework Interactions

Cross Species	P_0/k_B(K)	p_1	p_2 (Å)
H—O_z^{Si}	16113.4	6.3457	1.1239
H—O_z^{Al}	16113.4	6.3457	1.1239

Here Morse potential is defined as (Demiralp et al, *Phys. Rev. Lett.* 1999, 82, 1708):

$$U=p_0[e^{p1*(1-r/p2)}-2e^{(p1/2)*(1-r/p3)}]$$

During molecular simulations of adsorption isotherms, framework atoms may be fixed and extra-framework cations may be allowed to move (see e.g. Fang et al., *Phys Chem. Chem. Phys.,* 2013, 15, 12882). The positions of extra-framework cations can have a significant impact on the adsorption properties. For most cationic zeolites, however, the experimental information for cation locations is not available. To get more reliable cation distributions for each material, pre-equilibration simulations prior to the adsorption of CO_2 may be performed. Parallel tempering (also known as canonical replica-exchange Monte Carlo) may be used in these simulations. For each cationic material, replicas (e.g., 9) may be included in simulations at temperatures, such as 300K, 390K, 507K, 659K, 857K, 1114K, 1448K, 1882K and 2447K, respectively. The lowest temperature may be room temperature, and the highest temperature should be high enough so as to ensure that no replicas become trapped in local energy minima. Reasonable degree of overlap between the potential energy distributions of neighboring state points was found.

Adsorption isotherms of CO_2 in zeolites may be predicted computationally using standard Grand Canonical Monte Carlo (GCMC) methods. The chemical potential may be determined from the fugacity, and the fugacity coefficients may be computed using the Peng-Robinson equation of state (Peng and Robinson *Ind. Eng. Chem. Fundam.* 1976, 15, 59). Isosteric heats of adsorption, Q_{st}, defined as the difference in the partial molar enthalpy of the adsorption between the gas phase and the adsorbed phase, may be determined. Some topologies, for example, FAU and LTA, include regions such as sodalite cages that are inaccessible for CO_2 molecules. These regions may be blocked in the simulations to avoid spurious adsorption of CO_2 in these regions.

Accessible pore volume, which is defined as the percentage of the pore volume to the total volume of the zeolite, may be computed from Widom particle insertion using Helium. For the calculations of pore volumes, the Clay Force Field (CLAYFF) may be used for the atoms of the zeolite and force field parameters from the previous work may be used for He—He interactions (See Cygan et al., *J. Phys. Chem. B,* 2004, 108, 1255; Talu et al. *Colloids and Surfaces a-Physicochemical and Engineering Aspects,* 2001, 187, 83). Lorentz-Berthelot mixing rules may be applied for the cross species interactions.

Prototypical processes may be defined for CO_2 capture. For example, the following processes such as in Table 3 may be modeled. It understood that CO_2 adsorption processes are not limited to processes considered in Table 4.

TABLE 4

Processes Considered

	Adsorption		Desorption	
Processes	T (K)	P (bar)	T (K)	P (bar)
PSA1	300	5	300	1
PSA2	300	20	300	1
PSA3	300	0.066	300	0.0026
PSA4	233	0.066	233	0.0026
PTSA1	300	5	373	1
PTSA2	300	20	373	1
VSA	300	1	300	0.1
VTSA1	300	1	373	0.1
VTSA2	300	1	473	0.2
VTSA3	300	5	473	0.2
TSA	300	1	473	1

The choice of adsorption and desorption conditions may vary and be based on previous research and industrial relevance. The conditions in Table 3 are representative of only several possible set of conditions. Detailed process modeling of gas capture may require a description of multi-component adsorption of the gas mixtures of interest. As a first step, it may be sufficient to focus simply on the capacity a material has for the primary component of interest (e.g., CO_2). For example, zeolites as potential adsorbents for CO_2 may be considered based on single-component adsorption of CO_2.

For each process the working capacity (ΔN), which is defined as the difference between the adsorbed amounts of CO_2 at the adsorption (N_{ads}) and desorption (N_{des}) conditions, may be used to evaluate adsorption performance of the materials. Thus, via molecular simulations using the first-principles-derived force fields, the relationship between CO_2 working capacity and Si/Al ratio and cation concentration (e.g., sodium cation, potassium cation) may be determined for each zeolite framework structure at each defined process condition. For each framework structure, the optimal composition may be determined for each specified process. The optimal compositions for selected processes in Table 4 are shown below in Table 5.

TABLE 5

Examples Of Working Capacity Of The Optimal Compositions For Selected Zeolite Topologies In The Four CO_2 Adsorption Processes

PSA1		VSA		PTSA1		VTSA1	
Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)
RWY_5_100	6.49	RWY_3_17	5.34	RWY_3_17	11.17	IRY_2_0	8.78
IRY_10_100	4.98	IRY_3_83	4.48	IRY_3_0	8.68	IRR_2_0	7.82

TABLE 5-continued

Examples Of Working Capacity Of The Optimal Compositions For Selected Zeolite Topologies In The Four CO_2 Adsorption Processes

PSA1		VSA		PTSA1		VTSA1	
Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)	Zeolite	ΔN (mmol/cc)
FAU_50_67	4.40	FAU_5_100	4.28	IRR_5_50	7.76	FAU_2_33	7.51
TSC_50_83	4.36	IRR_3_100	3.79	FAU_5_83	7.12	EMT_2_0	7.26
IRR_10_100	4.25	EMT_5_83	3.78	TSC_10_17	6.87	RWY_3_17	7.14
EMT_50_100	4.12	VFI_1_0	3.52	EMT_5_33	6.74	TSC_1_0	6.60
LTA_50_67	3.75	RRO_Si	3.43	VFI_1_0	6.38	LTA_1_0	5.93
VFI_10_100	3.46	DAC_Si	3.39	LTA_10_33	5.87	VFI_2_0	5.31
SFF_Si	3.14	LTA_5_50	3.30	STF_Si	5.50	STF_5_0	5.24
STF_Si	3.13	TSC_5_0	3.27	DAC_Si	5.42	SFF_3_0	5.05
MWW_Si	2.91	STF_50_100	3.13	RRO_Si	5.06	MWW_2_33	4.87
ITH_Si	2.50	HEU_Si	2.84	SFF_50_100	4.94	STI_2_0	4.82
NES_Si	2.39	MWW_10_100	2.72	MWW_25_100	4.90	DAC_50_17	4.75
TUN_Si	2.32	SFF_25_67	2.69	ITH_Si	4.22	RRO_10_83	4.57
TER_Si	2.24	TER_50_100	2.31	TER_Si	4.20	NES_2_0	4.47
FER_Si	2.23	STI_10_83	2.29	STI_10_100	4.18	HEU_25_17	4.11
MFS_Si	2.19	MFS_25_100	2.25	NES_50_100	4.15	MFS_10_17	4.04
IMF_Si	2.09	TUN_50_100	2.23	TUN_Si	4.10	FER_10_33	3.79
STI_Si	2.08	NES_10_67	2.22	HEU_Si	4.07	SZR_5_67	3.77
SZR_Si	1.95	FER_50_100	2.18	FER_Si	4.05	EUO_3_0	3.77
MFI_Si	1.92	ITH_25_100	2.17	MFS_Si	3.97	ITH_10_17	3.74
EUO_Si	1.88	LAU_Si	2.15	LAU_Si	3.81	TER_10_17	3.66
DAC_Si	1.81	MFI_50_100	2.13	MFI_Si	3.79	TUN_10_67	3.60
LAU_Si	1.81	SZR_50_83	2.05	SZR_Si	3.78	LAU_10_0	3.44
RRO_Si	1.59	EUO_25_100	1.98	IMF_Si	3.78	MFI_10_33	3.34
TON_Si	1.48	IMF_50_100	1.96	EUO_25_100	3.58	IMF_10_0	3.28
MTT_Si	1.41	TON_Si	1.95	TON_Si	3.32	MTT_10_83	2.60
HEU_50_100	1.21	MTT_Si	1.59	MTT_Si	2.89	TON_25_0	2.46

[a] To describe the materials, we use ZEO_A_B to represent cationic zeolites, where ZEO indicates the topology type, A the Si/Al ratio, and B the percentage concentration of K cations. For siliceous zeolites, we use ZEO_Si.

The zeolite materials described herein may be represented by the following formula ZEO_A_B, wherein "ZEO" represents the framework structure, "A" represents the Si/Al ratio and "B" represents the concentration of potassium cations. For example, MFI_10_50 represents a zeolite material having an MFI framework structure, a Si/Al ratio of 10 and a potassium cation concentration of 50%. MFI_Si represents a zeolite material having an MFI framework structure that is highly siliceous. As used herein, "highly siliceous" refers to a zeolite material having a Si/Al ratio of ≥about 100, ≥about 150, ≥about 200, ≥about 250, ≥about 300, ≥about 350, ≥about 400≥about 450, ≥about 500, ≥about 550, ≥about 600, ≥about 650, ≥about 700, ≥about 750, ≥about 800, ≥about 850, ≥about 900, ≥about 950, or ≥about 1000. In particular, a highly siliceous zeolite has a Si/Al ratio of above 100. Such highly siliceous zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Also, it has been found that a substantially linear relationship between working capacity and accessible pore volume exists for the optimal compositions of the framework structures for the processes studied, as shown in FIG. **2** for the PSA1 process. It was further found that the average Q_{st} are located within a narrow range for each process, as shown in FIG. **3** for the PSA1 process. In contrast, the heats of adsorption at zero coverage (Q_{st}^0) are located in a relatively larger range for each process. The results indicated that suitable average Q_{st} are required for maximizing the working capacity of each topology in a specified process. Too high an average Q_{st} may lead to a large amount of residual adsorbed adsorbate at the desorption pressure, and therefore to a reduced working capacity, whereas too low an average Q_{st} may also result in a low working capacity. As a result, for each topology there is an optimal average Q_{st} for obtaining the maximum working capacity.

Thus, in various aspects, a method of designing zeolites for CO_2 adsorption involves identifying a target adsorption process for CO_2. Any suitable CO_2 adsorption process known in the art may be targeted. Non-limiting examples of suitable CO_2 adsorption processes include pressure swing adsorption (PSA), temperature swing adsorption (TSA), pressure temperature swing adsorption (PTSA), vacuum swing adsorption (VSA), vacuum temperature swing adsorption (VTSA), partial pressure swing adsorption (PPSA), partial pressure temperature swing adsorption (PPTSA), and displacement desorption swing adsorption (DDSA), and any other combinations thereof. Once the CO_2 adsorption process is identified, zeolite framework structure may be selected. In particular, zeolite framework structures with large accessible pore volumes from 0.15 and higher may be selected. Examples of suitable zeolite framework structures include but are not limited to AFT, AFX, CAS, CHA, DAC, EMT, EUO, FAU, FER, HEU, IMF, IRR, IRY, ITH, ITT, KFI, LAU, LTA, MFI, MFS, MRE, MTT, MWW, NES, PAU, RHO, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, UFI, and VFI. A person of ordinary skill in the art knows how to make the zeolites having an aforementioned framework structure. For example, see the references provided in the International Zeolite Association's database of zeolite structures found at www.iza-structure.org/databases.

Following selection of a zeolite framework, the Si/Al ratio may be adjusted in order to arrive at a heat of adsorption (Q_{st}) that results in a high CO_2 working capacity (ΔN) for zeolite material in the identified CO_2 adsorption process. As used herein, a "high working capacity" or "high AN" may be ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Examples of suitable Si/Al ratios include, but are not limited to about 1, about 2, about 3, about 5, about 9, about 10, about 15, about 20, about 25, about 30, about 35, about 40, about 45, about 50, about 55, about 60, about 65, about 70, about 75, about 80, about 85, about 90, about 95, or about 100. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 1 to about 100, about 3 to about 100, about 1 to about 75, about 1 to about 20, about 1 to about 10, about 9 to about 85, about 9 to about 70, about 5 to about 45, about 40 to about 60, about 3 to about 100, about 3 to about 75, about 5 to about 60, about 3 to about 60, about 3 to about 30, etc.

Additionally, cations may be introduced into the zeolite material at varying concentrations to arrive at a high CO_2 working capacity for the zeolite material. The concentration of cations is the percentage of specific cations to the total number of positively charged extra framework cations and protons, which are required to balance the charge in the specific zeolite framework. Examples of suitable cations include, but are not limited to potassium cations (K^+), sodium cations (Na^+), lithium cations (Li^+), cesium cations (Cs^+), rubidium cations (Rb^+), silver cations (Ag^+), calcium cations (Ca^{2+}), magnesium cations (Mg^{2+}), barium cations (Ba^{2+}), strontium cations (Sr^{2+}), copper cations (Cu^{2+}), and protons (H^+). For example, the zeolite material may have a cation (e.g., potassium cation, sodium cation) concentration of ≥about 0.0%, ≥about 5.0%, ≥about 10.0%, ≥about 15.0%, ≥about 16.7%, ≥about 20.0%, ≥about 25.0%, ≥about 30.0%, ≥about 33.4%, ≥about 35.0%, ≥about 40.0%, ≥about 45.0%, ≥about 50.0%, ≥about 55.0%, ≥about 60.0%, ≥about 65.0%, ≥about 66.7%, ≥about 70.0%, ≥about 75.0%, ≥about 80.0%, ≥about 83.3%, ≥about 85.0%, ≥about 90.0%, ≥about 95.0%, or about 100%. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 0.0% to about 100%, about 1.0% to about 100%, about 5.0% to about 100%, about 10% to about 100%, about 0.0% to about 90.0%, about 0.0% to about 40.0%, about 40.0% to about 100%, about 0% to about 50%, about 5% to about 40%, etc. In particular, the Si/Al ratio may be adjusted in the zeolite material before the introduction of cations. Once the desired zeolite material is designed, experimental testing may be undergone on the zeolite material where other factors, such as energy costs for adsorbent regeneration, adsorption kinetics, etc., may be considered.

III. CO_2 Adsorption Processes

In another embodiment, a CO_2 adsorption process is provided herein. The CO_2 adsorption process comprises contacting a gas mixture containing CO_2 with an adsorbent material, wherein the adsorbent material may be designed according to the description above.

In various aspects, the CO_2 adsorption process can be achieved by swing adsorption processes, such as pressure swing adsorption (PSA) and temperature swing adsorption (TSA) and combinations thereof (e.g., pressure temperature swing adsorption (PTSA)). All swing adsorption processes have an adsorption step in which a feed mixture (typically in the gas phase) is flowed over an adsorbent that preferentially adsorbs a more readily adsorbed component relative to a less readily adsorbed component. A component may be more readily adsorbed because of kinetic or equilibrium properties of the adsorbent material.

PSA processes rely on the fact that gases under pressure tend to be adsorbed within the pore structure of the adsorbent materials. Typically, the higher the pressure, the greater the amount of targeted gas component that will be adsorbed. When the pressure is reduced, the adsorbed targeted component is typically released, or desorbed. PSA processes can operate across varying pressures. For example, a PSA process that operates at pressures below atmospheric pressure is a vacuum swing adsorption (VSA) process. PSA processes can be used to separate gases of a gas mixture, because different gases tend to fill the pores or free volume of the adsorbent to different extents due to either the equilibrium or kinetic properties of the adsorbent. In many important applications, to be described as "equilibrium-controlled" processes, the adsorptive selectivity is primarily based upon differential equilibrium uptake of the first and second components. In another important class of applications, to be described as "kinetic-controlled" processes, the adsorptive selectivity is primarily based upon the differential rates of uptake of the first and second components.

TSA processes also rely on the fact that gases under pressure tend to be adsorbed within the pore structure of the adsorbent materials. When the temperature of the adsorbent is increased, the adsorbed gas is typically released, or desorbed. By cyclically swinging the temperature of adsorbent beds, TSA processes can be used to separate gases in a mixture when used with an adsorbent selective for one or more of the components in a gas mixture. Partial pressure purge displacement (PPSA) swing adsorption processes regenerate the adsorbent with a purge. Rapid cycle (RC) swing adsorption processes complete the adsorption step of a swing adsorption process in a short amount of time. For kinetically selective adsorbents, it can be preferable to use a rapid cycle swing adsorption process. If the cycle time becomes too long, the kinetic selectivity can be lost. These swing adsorption protocols can be performed separately or in combinations. Examples of processes that can be used herein either separately or in combination are PSA, TSA, PTSA, VSA, VTSA, PPSA, PPTSA DDSA.

Additionally or alternatively, the processes of the present invention can comprise an adsorption step in which the preferentially adsorbed components (e.g., CO_2) of the feed mixture can be adsorbed by the adsorbent material described herein as contained in an adsorbent contactor, such as an adsorbent bed, while recovering the less preferentially adsorbed components at the product end of the adsorbent bed at process pressures. The adsorption step may be performed at a first pressure such that the partial pressure of CO_2 is from about 0.5 bar to about 25 bar, particularly about 3 bar to about 25 bar, particularly about 15 bar to about 25 bar, particularly about 3 bar to about 10 bar, particularly about 0.5 bar to about 7 bar, or particularly about 0.5 bar to about 3 bar. Additionally or alternatively, the adsorption step of the present invention can be performed at a first temperature from about −20° C. to about 80° C., particularly from about 0° C. to about 50° C. or particularly from 10° C. to 30° C. Additionally or alternatively, heat of adsorption can be managed by incorporating a thermal mass into the adsorption bed to mitigate the temperature rise occurring during the adsorption step. The temperature rise from the heat of adsorption can additionally or alternately be managed in a variety of ways, such as by flowing a cooling fluid through the passages external to the adsorbent bed (i.e., the passages that are used to heat and cool the contactor).

Additionally or alternatively, the passages external to the adsorbent bed can be filled with a fluid that is not flowing during the adsorption process. In this case, the heat capacity of the fluid can serve to mitigate the temperature rise in the adsorbent bed. Combinations of some or all of these heat management strategies can be employed. Even with these heat management strategies, during this step, the final temperature of the bed can typically be slightly higher than the feed inlet temperature. Particularly, the degree of adsorption and cooling can be managed so that the maximum temperature rise at any point within the contactor can be less than about 40° C., e.g., less than about 20° C., less than about 10° C., or less than about 5° C. During adsorption, the strongest-adsorbing components can tend to attach most strongly to the adsorbent and can thus be least mobile. Such strongest-adsorbing components can thus tend to occupy regions of adsorbent closest to the inlet and can generally displace weakly adsorbed components from those regions.

Over the period of adsorption, the adsorbates can tend to order themselves from strongest to weakest, moving from inlet to outlet of the adsorption channels of the contactor. In preferred embodiments, the feed gas velocity can be chosen so that a relatively sharp concentration front moves through the contactor, i.e., such that the concentration gradient of adsorbate(s) extends over a relatively short distance, taking into consideration the absolute amplitude of the gradient.

The adsorption step can be stopped at a predetermined point before the adsorption front breaks through the product output end of the adsorbent bed. The adsorption front can move at least 30% of the way down the bed, e.g., at least 50% or at least 80%, before the adsorption step is stopped. Additionally or alternatively, the adsorption step can be conducted for a fixed period of time set by the feed flow rate and adsorbent capacity. Further additionally or alternatively, the adsorption step can be conducted for a time less than 600 seconds, particularly less than 120 seconds, e.g., less than 40 seconds or less than 10 seconds, or less than 5 seconds. In some instances, the adsorption front can be allowed to break through the output end only for a short duration (e.g., for at most a few seconds), but usually the adsorption front is not allowed to break through, which can maximize utilization of the bed.

After the adsorption step, the feed gas channels in the contactor can optionally be depressurized to a second pressure lower than the first pressure. For example, the second pressure may be such that the partial pressure of CO_2 is from about 0.5 bar to about 2 bar, particularly about 0.05 bar to about 0.5 bar, particularly about 0.08 bar to about 0.3 bar, or particularly about 0.09 bar to about 0.4 bar. Reduction in pressure to a second pressure may be achieved by passing a purge gas, substantially free of target gas species (e.g., CO_2) through adsorbent bed. The purge gas may comprise an inert gas, such as nitrogen.

Additionally or alternatively, the feed input end of the adsorbent bed can be sealed with respect to the passage of a gas, and heat can be externally applied to the adsorbent bed. By "externally heated" it is meant that heat is not applied directly to the adsorbent bed through the flow channels through which the feed gas mixture had flowed and into which the target gas component will be desorbed. The heat can be delivered to the adsorbent bed through a plurality of heating/cooling channels in thermal communication, but not in fluid communication, with the feed gas flow channels of the adsorbent. The adsorbent bed can be externally heated co-currently or counter-currently along its length with respect to the flow of the feed gas mixture, or in a combination of co-current and counter-current heating steps. The flow channels that will carry heating and cooling fluid can be in physical contact with the adsorbent bed to enhance heat transfer. The adsorbent bed can be heated to a second temperature higher than the first temperature used during the adsorption step, the second temperature at least about 10° C. higher than the first temperature, e.g., at least about 20° C. higher, at least about 40° C. higher, at least about 75° C. higher, at least about 90° C. higher, at least about 100° C. higher, at least about 125° C. higher, at least about 150° C. higher, at least about 175° C. higher or at least about 200° C. higher; additionally or alternatively, the second temperature can be from about 50° C. to about 250° C., e.g., from about 150° C. to 250° C., from about 50° C. to about 150° C., from about 75° C. to about 125° C. or from about 175° C. to about 225° C.

During the heating step, the gas pressure in the channel can tend to rise. To improve regeneration at the product end of the bed, during the heating step, the bed can advantageously be slowly purged with clean gas from the clean end (product end) of the adsorbent bed to the point of product recovery. By "clean gas" it is meant that a gas is substantially free of target gas components. For example, if the target gas is CO_2, then the clean gas will be a stream substantially CO_2. In one embodiment, clean gas will contain less than 5 mol % CO_2, and particularly less than 1 mol % of CO_2. An example of a suitable clean gas would be the product gas itself. When the current invention is utilized for the removal of CO_2 from a natural gas stream, in one embodiment, the "clean gas" is comprised of at least one of the hydrocarbon product streams, and in another embodiment is comprised of C_3-hydrocarbons, and in another embodiment is comprised of methane. In other embodiments, a separate "clean gas" can be used. In one of these embodiments, the "clean gas" is comprised of nitrogen.

The purge can be introduced at a pressure higher than the pressure in the adsorbent bed. It can be preferred for the total number of moles of purge gas introduced to be less that the number of moles of molecules adsorbed in the contactor, e.g., less than 25% or less that 10% of the number of moles adsorbed. By preventing the adsorption front from breaking through, the product end of the bed can be kept substantially free of the strongly-adsorbed species and can advantageously contain predominantly product species. The isotherms of the adsorbed target component can determine the partial pressure of the preferentially adsorbed component in equilibrium, with the new loading at the higher temperature. This partial pressure can, in some cases, be in excess of 40% greater than the feed pressure, or as much as 70% higher or more. Additionally or alternatively to the recovered sensible heat, a small amount of extra heat may be required to heat the bed to the final predetermined temperature. The isotherm can describe the amount of loading (mmol of adsorbed species per gram of adsorbent) for both chemisorption and physisorption processes.

The external heating can be conducted such that a thermal wave is used to pass heat through the contactor, as it transitions from the adsorption step to the regeneration step, in transitioning from the regeneration to adsorption step, in at least part of the regeneration step, and/or in at least part of the adsorption step. Similarly, it can be preferred to utilize a thermal wave in the cooling step. A thermal wave is a relatively sharp temperature gradient, or front, that can move linearly (i.e., approximately in a single direction within the contactor) during at least one step in the thermal swing adsorption/desorption cycle. The speed at which the thermal front (i.e., region with sharp temperature gradient) can move is referred to as the thermal wave velocity. The thermal wave velocity need not be constant, and the thermal wave direction need not be the same in both adsorption and regeneration steps. For example, the wave can move co-currently, counter-currently, or cross-flow in the adsorption and/or regeneration steps. It is also possible to design a process in which there is no significant thermal wave present in the adsorption step while there is a significant thermal wave in the regeneration step. The presence of a thermal wave in at least some portion of the thermal swing adsorption/regeneration cycle can enable the overall system to achieve a goal of substantially recuperating and recovering the heat required to temperature-swing the adsorbent bed. This, in turn, can improve process efficiency and/or can enable the use of high desorption temperatures that would not normally be considered for TSA operation.

Additionally or alternatively, the contactor is combined with the adsorbent material into a heat exchange structure in a manner that can produce a thermal wave. In Thermal Wave Adsorption (TWA), adsorbent can be placed in one set of heat exchanger channels, while the other set of channels can be used to bring heat into and/or take heat out of the adsorbent device. Fluids and/or gases flowing in the adsorbent and heating/cooling channels do not generally contact each other. The heat adding/removing channels can be designed and operated in a manner that results in a relatively sharp temperature wave in both the adsorbent and in the heating and cooling fluids during the heating and cooling steps in the cycle. An example of a contactor that can produce a relatively sharp thermal wave is a contactor as described herein.

Relatively sharp thermal waves, as used herein, can be expressed in terms of a standard temperature differential over a distance relative to the length of the mass/heat transfer flow in the apparatus. With respect to the mass/heat transfer, we can define a maximum temperature, T_{max}, and a minimum temperature, T_{min}, as well as convenient temperatures about 10% above T_{min} (T_{10}) and about 10% below T_{max} (T_{90}). Thermal waves can be said to be relatively sharp when at least the temperature differential of ($T_{90}-T_{10}$) occurs over at most 50% (e.g., at most 40%, at most 30%, or at most 25%) of the length of the apparatus that participates in the mass/thermal transfer. Additionally or alternatively, relative sharp thermal waves can be expressed in terms of a maximum Peclet number, Pe, defined to compare axial velocity of the heating/cooling fluid to diffusive thermal transport roughly perpendicular to the direction of fluid flow. Pe can be defined as $(U^*L)/\alpha$, where U represents the velocity of the heating/cooling fluid (in m/s), L represents a characteristic distance over which heat is transported (to warm/cool the adsorbent) in a direction roughly perpendicular to the fluid flow, and a represents the effective thermal diffusivity of the contactor (in m^2/s) over the distance L. In addition or alternately to the thermal differential over length, thermal waves can be said to be relatively sharp when Pe is less than 10, for example less than 1 or less than 0.1. To minimize time for heating/cooling of the contactor with little or no damage to the flow channel, it can be preferred for U to be in a range from about 0.01 m/s to about 100 m/s, e.g., from about 0.1 m/s to about 50 m/s or from about 1 m/s to about 40 m/s. Additionally or alternatively, to minimize size and energy requirements, it can be preferred for L to be less than 0.1 meter, e.g., less than 0.01 meter or less than 0.001 meter.

Thermal waves in such contactors can be produced when the heating and cooling fluids are flowed co-current or counter-current to the direction of the feed flow in the adsorption step. In many cases, it can be preferred not to have a significant flow of heating or cooling fluids during the adsorption step. A more comprehensive description of Thermal Wave Adsorption (TWA) and other appropriate contactor structures can be found, e.g., in U.S. Pat. No. 7,938,886, which is incorporated herein by reference. This reference shows how to design and operate a contactor to control the sharpness and nature of a thermal wave. A key operational parameter can include the fluid velocity in the contactor. Key design parameters can include the mass of the contactor and heat capacity and thermal conductivity of materials used to form the contactor and heat transfer fluid. An additional key design objective for the contactor can be finding one or more ways to reduce/minimize the distance over which heat has to be transferred, which is why relatively sharp thermal waves can be so desirable.

Additionally or alternatively, during the heating step, the volume of fluid at a temperature no more than 10° C. warmer than the end of the contactor from which it is produced can represent at least 25% (e.g., at least 50% or at least 75%) of the volume of the fluid introduced into the contactor for heating. Similarly, when the present invention is operated to attain a thermal wave, it can be preferred that, during the cooling step, a cold fluid (such as pressurized water) can be flowed into the contactor and a hot fluid near the temperature of the contactor at the end of the recovery step can flow out of the contactor. Most of the recovery step can generally occur after the contactor has been heated. Thus additionally or alternatively during the cooling step, the volume of fluid at a temperature no more than 10° C. colder than the end of the contactor from which it is produced can represent at least 25% (e.g., at least 50% or at least 75%) of the volume of the fluid introduced into the contactor for cooling.

One way to efficiently utilize thermal waves in the apparatuses according to the invention can be for heat recovery. The recovered energy can be used to reduce the energy requirements for heating and cooling of the contactor, for a different contactor of a multitude of contactors needed for a continuous process, and/or for any other purpose. More specifically, energy contained in the hot stream exiting the contactor during the cooling step can be utilized to reduce the energy that must be supplied during the heating step. Similarly, the cold stream exiting the contactor during the heating step can be utilized to reduce the energy that must be supplied to cool fluid to be supplied to the contactor during the cooling step. There are many ways to recoup the energy. For example, the hot thermal fluid flowing out of one contactor can be sent to another with trim heating in between, and/or the cold fluid flowing out of one contactor can be sent to another with trim cooling in between. The thermal fluid flow path between contactors can be determined by valves timed to route thermal fluid between contactors at appropriate points in the overall swing adsorption cycle. In embodiments where thermal fluid flows between contactors, it may also pass through a heat exchanger that adds or removes heat from the flowing thermal fluid and/or pass through a device, such as a compressor, pump, and/or blower, that pressurizes it so it can flow at the desired rate though the contactors. A heat storage medium can be configured so that the energy from the thermal wave moving through one contactor can be stored. A non-limiting example is a tank system that separately stores hot and cold fluids, which can each be fed back into the contactor that produced it and/or to another contactor. In many embodiments, the flow of the thermal fluid through the contactor can be arranged to minimize the mixing of the fluid in the direction of the general flow of the fluid through the contactor and to minimize the effect of the thermal conductivity of the fluid on the sharpness of the temperature wave.

Where energy is recovered, the recovered energy can be used to reduce the amount of sensible heat that must be supplied to heat and cool the contactor. The sensible heat is determined by the heat capacity and temperature rise (or fall) of the contactor. In some embodiments, at least 60% (e.g., at least 80% or at least 95%) of the sensible heat required for heating the contactor is recouped, and/or at least 60% (e.g., at least 80% or at least 95%) of the sensible heat needed to cool the contactor is recouped.

This external heating of the partially sealed adsorbent bed will result in at least a portion of the target species being desorbed from the adsorbent bed. It can also result in an increase in pressure of the resulting target species component stream. At least a portion of the desorbed target species component is recovered at pressures higher than that at the initiation of the heating step. That is, recovery of target gas will take place toward the end of the heating step with minimum or no depressurization of the adsorbent bed. It is preferred that the pressure be a least 2 bar, particularly at least 5 bar higher than that at the initiation of the heating step.

The pressure in the adsorbent bed is then reduced, particularly in a series of blow-down steps in a co-current or counter-current and can be performed with or without a purge gas stream to the final target gas recovery pressure. Pressure reduction can occur in less than 8 steps, particularly in less than 4 steps, with target species being recovered in each step. In one embodiment, the pressure is decreased by a factor of approximately three in each step. It is also preferred that the depressurization be conducted counter-currently and that during the depressurizing step a purge gas be passed counter-current (from product end to feed end) through the adsorbent bed. It is also preferred that the purge gas be a so-called clean gas as previously described.

In another embodiment, in any step, other than the adsorption step, the clean gas is conducted counter-currently through the adsorbent bed to ensure that the end of the bed is substantially free of target species. In another embodiment, the clean gas is conducted counter-currently through the adsorbent bed in at least a portion of the desorption steps. An effective rate of counter-current flowing clean gas is preferred during these step(s) to overcome mass diffusion to ensure that the product end of the bed is kept substantially free of the target species.

After the target gas has been recovered, the adsorbent bed can be cooled and repressurized. One can cool the bed before repressurization. The adsorbent bed can be cooled, particularly to a temperature that is no more than 40° C. above the temperature of feed gas mixture, e.g., no more than 20° C. above or no more than 10° C. above. Additionally or alternatively, the adsorbent bed can be cooled by external cooling in a co-current or counter-current manner, such that a thermal wave can pass through the bed. In some such embodiments, the first part of the adsorbent bed can be cooled then repressurized. In certain of those embodiments, less than 90% of the length of adsorption bed can be cooled, e.g., less than 50%. The adsorbent bed can additionally or alternatively be purged with a clean gas during cooling.

The adsorbent bed can then be repressurized, during and/or after the cooling step, e.g., using clean product gas or counter-currently with blow-down gas from another bed after a first stage of repressurization. The final pressure of the repressurization step can be substantially equal to the pressure of the incoming feed gas mixture.

The adsorbent be can be in the form of open flow channels, e.g., parallel channel connectors, in which the majority of the open pore volume is attributable to microporous pore diameters, e.g., in which less than 40%, particularly less than 20%, for example less than 15% or less than 10%, of its open pore volume can originate from pore diameters greater than 20 angstroms (and less than about 1 micron; i.e., from mesoporous and macroporous pore diameters).

A flow channel is described herein as that portion of the contactor in which gas flows if a steady state pressure difference is applied between the point/place at which a feed stream enters the contactor and the point/place a product stream leaves the contactor. By "open pore volume" herein, it is meant all of the open pore space not occupied in the volume encompassed by the adsorbent material. The open pore volume includes all open spaces in the volume encompassed by the adsorbent material, including but not limited to all volumes within the adsorbent materials themselves, including the pore volume of the structured or amorphous materials, as well as any interstitial open volumes within the structure of the portion of the bed containing the adsorbent material. Open pore volume, as used herein, does not include spaces not accompanied by the adsorbent material such as open volumes in the vessel for entry, exit, or distribution of gases (such as nozzles or distributor areas), open flow channels, and/or volumes occupied by filler materials and/or solid heat adsorption materials. "Parallel channel contactors" are defined herein as a subset of adsorbent contactors comprising structured (engineered) adsorbents in which substantially parallel flow channels are incorporated into the adsorbent structure (typically the adsorbents can be incorporated onto/into the walls of such flow channels). Non-limiting examples of geometric shapes of parallel channel contactors can include various shaped monoliths having a plurality of substantially parallel channels extending from one end of the monolith to the other; a plurality of tubular members, stacked layers of adsorbent sheets with and without spacers between each sheet; multi-layered spiral rolls; spiral wound adsorbent sheets; bundles of hollow fibers; as well as bundles of substantially parallel solid fibers; and combinations thereof. Parallel flow channels are described in detail, e.g., in U.S. Patent Application Publication Nos. 2008/0282892 and 2008/0282886, both of which are incorporated herein by reference. These flow channels can be formed by a variety of ways, and, in addition to the adsorbent material, the adsorbent contactor structure may contain items such as, but not limited to, support materials, heat sink materials, void reduction components, and heating/cooling passages.

It can be desirable to operate with a multiplicity of contactor units, with several coupled in a heating/cooling operation and others involved in adsorption (and/or desorption). In such an operation, the contactor can be substantially cooled by a circulating heat transfer medium before it is switched into service for adsorption. One advantage of such an operation can be that the thermal energy used to swing the bed is retained in the heat transfer medium. If adsorption were to proceed simultaneously with cooling, then a substantial part of the heat in the bed could be lost to the adsorbate-free feed, and a higher heat load could be needed to restore the high temperature of the heat transfer medium.

In various aspects, the adsorbent material selective for adsorbing CO_2 in the adsorption processes described herein may comprise a zeolite with a framework structure selected from group consisting of AFT, AFX, CAS, CHA, DAC, EMT, EUO, FAU, FER, HEU, IMF IRR, IRY, ITH, ITT, KFI, LAU, LTA, MFI, MFS, MRE, MTT, MWW, NES, PAU, RHO, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, UFI and VFI. Additionally or alternatively, in combination with the aforementioned framework structures, the zeolite may have a Si/Al ratio of ≥about 1, ≥about 2, ≥about 3, ≥about 5, ≥about 9, ≥about 10, ≥about 15, ≥about 20, ≥about 25, ≥about 30, ≥about 35, ≥about 40, ≥about 45, ≥about 50, ≥about 55, ≥about 60, ≥about 65, ≥about 70, ≥about 75, ≥about 80, ≥about 85, ≥about 90, ≥about 95, ≥about 100, ≥about 150, ≥about 200, ≥about 250, ≥about 300, ≥about 350, ≥about 400≥about 450, ≥about 500, ≥about 550, ≥about 600, ≥about 650, ≥about 700, ≥about 750, ≥about 800, ≥about 850, ≥about 900, ≥about 950, or ≥about 1000. Additionally or alternatively, in combination with the aforementioned framework structures, the zeolite may have a Si/Al ratio of ≤about 1, ≤about 2, ≤about 3, ≤about 5, ≤about 9, ≤about 10, ≤about 15, ≤about 20, ≤about 25, ≤about 30, ≤about 35, ≤about 40, ≤about 45, ≤about 50, ≤about 55, ≤about 60, ≤about 65, ≤about 70, ≤about 75, ≤about 80, ≤about 85, ≤about 90, ≤about 95, ≤about 100, ≤about 150, ≤about 200, ≤about 250, ≤about 300, ≤about 350, ≤about 400≤about 450, ≤about 500, ≤about 550, ≤about 600, ≤about 650, ≤about 700, ≤about 750, ≤about 800, ≤about 850, ≤about 900, ≤about 950, or ≤about 1000. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 1 to about 1000, about 5 to about 100, about 10 to about 90, about 1 to about 70, about 3 to about 85, etc.

Additionally or alternatively, in combination with the aforementioned framework structures and/or Si/Al ratios, the zeolite may have a cation (e.g., potassium cations (K^+), sodium cations (Na^+), lithium cations (Li^+), cesium cations (Cs^+), rubidium cations (Rb^+), silver cations (Ag^+), calcium cations (Ca^{2+}), magnesium cations (Mg^{2+}), barium cations (Ba^{2+}), strontium cations (Sr^{2+}), copper cations (Cu^{2+}), and protons (H^+)) concentration of ≥about 0.0%, ≥about 5.0%, ≥about 10.0%, ≥about 15.0%, ≥about 16.7%, ≥about 20.0%, ≥about 25.0%, ≥about 30.0%, ≥about 33.4%, ≥about 35.0%, ≥about 40.0%, ≥about 45.0%, ≥about 50.0%, ≥about 55.0%, ≥about 60.0%, ≥about 65.0%, ≥about 66.7%, ≥about 70.0%, ≥about 75.0%, ≥about 80.0%, ≥about 83.3%, ≥about 85.0%, ≥about 90.0%, ≥about 95.0%, or about 100%. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 0.0% to about 100%, about 1.0% to about 100%, about 5.0% to about 100%, about 10% to about 100%, about 0.0% to about 40.0%, about 40.0% to about 100%, about 5% to about 40%, etc.

The zeolite may have a cation concentration comprising one or more cations. As understood herein, where the zeolite has a specific cation concentration of less than 100%, e.g., a potassium cation concentration of 50%, the zeolite may also contain at least one other cation such that the concentration of all the cations present totals about 100%. Thus, if the zeolite has a potassium cation concentration of about 50%, the zeolite may have one or more other cations at a concentration of about 50%, e.g., a sodium cation concentration of about 50%, a sodium cation concentration of about 25% and a lithium cation concentration of about 25%. In the case of a zeolite containing divalent cations (such as calcium cations (Ca^{2+}), magnesium cations (Mg^{2+}), barium cations (Ba^{2+}), strontium cations (Sr^2) and copper cations (Cu^{2+})) it is understood that the number of divalent cations required to balance the charge is twice smaller than the number of monovalent cations (such as potassium cations (K^+), sodium cations (Na^+), lithium cations (Li^+), cesium cations (Cs^+), rubidium cations (Rb^+), silver cations (Ag^+) or protons (H^+)). For example, if the zeolite has a potassium cation concentration of about 50%, the zeolite may have one or more other cations, e.g., a sodium cation concentration of about 50%, or calcium cation concentration of about 25%.

Details regarding specific processes for CO_2-adsorption are provided below.

A. Pressure Swing Adsorption (PSA) Processes

In another embodiment, a PSA process for separating CO_2 from a feed gas mixture is provided. The PSA process may include subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed. The feed gas mixture may be natural gas, syngas, flue gas as well as other streams containing CO_2. Typical natural gas mixtures contain CH_4 and higher hydrocarbons (C_2H_6, C_3H_8, C_4H_{10} etc), as well as acid gases (CO_2 and H_2S), N_2 and H_2O. The amount of water in the natural gas mixture depends on prior dehydration processing to remove H_2O. Typical syngas mixtures contain H_2, CO, CO_2, CH_4, COS and H_2S. Typical flue gas mixtures contain N_2, CO_2, H_2O, O_2, SO_2. The adsorbent bed may comprise a feed input end, a product output end and an adsorbent material selective for adsorbing CO_2. Additionally, the adsorbent bed may be operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed.

The first temperature may be ≥about −30° C., ≥about −25° C., ≥about −20° C., ≥about −15° C., ≥about −10° C., ≥about −5° C., ≥about 0° C., ≥about 5° C., ≥about 10° C., ≥about 15° C., ≥about 20° C., ≥about 25° C., ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., or ≥about 100° C. In particular, the first temperature may be ≥about 25° C. Additionally or alternatively, the first temperature may be ≤about −30° C., ≤about −25° C., ≤about −20° C., ≤about −15° C., ≤about −10° C., ≤about −5° C., ≤about 0° C., ≤about 5° C., ≤about 10° C., ≤about 15° C., ≤about 20° C., ≤about 25° C., ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., or ≤about 100° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about −30° C. to about 100° C., about −25° C. to about 95° C., about −20° C. to about 80° C., about 0° C. to about 50° C., about 10° C. to about 30° C. In particular, the first temperature is about −20° C. to about 80° C., about 0° C. to about 50° C. or about 10° C. to about 30° C.

The first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 may be ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 5 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, ≥about 10 bar, ≥about 12 bar, ≥about 15 bar, ≥about 16 bar, ≥about 18 bar, ≥about 20 bar, ≥about 22 bar, ≥about 24 bar, ≥about 25 bar, ≥about 26 bar, ≥about 28 bar, or ≥about 30 bar. In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≥about 5 bar or ≥about 25 bar. Additionally or alternatively, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 5 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, ≤about 10 bar, ≤about 12 bar, ≤about 15 bar,

≤about 16 bar, ≤about 18 bar, ≤about 20 bar, ≤about 22 bar, ≤about 24 bar, ≤about 25 bar, ≤about 26 bar, ≤about 28 bar, or ≤about 30 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 1 bar to about 30 bar, about 2 bar to about 28 bar, about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 15 bar to about 25 bar. In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 3 bar to about 7 bar, about 15 bar to about 25 bar, or about 18 bar to about 22 bar.

In various aspects, the PSA process may further include stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed, reducing the pressure in the adsorption bed to a second pressure, which may be lower than the first pressure, resulting in desorption of at least a portion of CO_2 from the adsorbent bed, and recovering at least a portion of CO_2 from the adsorbent bed. The second pressure may be such that the partial pressure of CO_2 is ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, or ≥about 10 bar. In particular, the second pressure may be such that the partial pressure of CO_2 is ≥about 1 bar. Additionally or alternatively, the second pressure may be such that the partial pressure of CO_2 is ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, or ≤about 10 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.1 bar to about 10 bar, about 0.3 bar to about 9 bar, about 0.5 bar to about 5 bar, about 0.5 bar to about 2 bar, about 1 bar to about 5 bar, etc. In particular, the second pressure may be such that the partial pressure of CO_2 is about 0.5 bar to about 2 bar, about 1 bar to about 5 bar, or about 0.9 bar to about 3 bar.

In various aspects, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a framework structure selected from the group consisting of AFT, AFX, DAC, EMT, EUO, IMF, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CAS, EMT, FAU, HEU, IRR, IRY, ITT, LTA, RWY, TSC and VFI, and a combination thereof, having (i) a Si/Al ratio of about 5 to about 100, about 5 to about 90, about 5 to about 85, about 5 to about 70 or about 5 to about 50; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 100%, about 5% to about 100%, about 10% to about 100%, about 40% to about 100%, about 60% to about 100% or about 70% to about 100%.

Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of LTA, TSC, and a combination thereof, having (i) a Si/Al ratio of about 40 to about 60 or about 50; and/or a (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 50% to about 90%, about 50% to about 80% or about 60% to about 70%.

Additionally or alternatively, the above mentioned adsorbent materials may not include a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO and a combination thereof.

Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio of between about 5 and about 45 (e.g., about 6, about 10, about 20, about 30, about 40, etc.) and with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof. Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio of between about 5 and about 45 (e.g., about 6, about 10, about 20, about 30, about 40, etc.) and with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may have a working capacity of ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Additionally or alternatively, the adsorbent material may have a working capacity of ≤about 1.0 mmol/cc, ≤about 2.0 mmol/cc, ≤about 3.0 mmol/cc, ≤about 4.0 mmol/cc, ≤about 5.0 mmol/cc, ≤about 6.0 mmol/cc, ≤about 7.0 mmol/cc, ≤about 8.0 mmol/cc, ≤about 9.0 mmol/cc, ≤about 10.0 mmol/cc, ≤about 11.0 mmol/cc, ≤about 12.0 mmol/cc, ≤about 13.0 mmol/cc, ≤about 14.0 mmol/cc, ≤about 15.0 mmol/cc, ≤about 16.0 mmol/cc, ≤about 17.0 mmol/cc, ≤about 18.0 mmol/cc, ≤about 19.0 mmol/cc, or ≤about 20.0 mmol/cc. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 1.0 mmol/cc to about 20.0 mmol/cc, about 1.0 mmol/cc to about 16.0 mmol/cc, about 2.0 mmol/cc to about 15.0 mmol/cc, about 3.0 mmol/cc to about 12.0 mmol/cc, etc. In particular, the adsorbent material described herein may have a working capacity of about 2.0 mmol/cc to about 15.0 mmol/cc or about 3.0 mmol/cc to about 12.0 mmol/cc.

Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≥about 15 kJ/mol, ≥about 16 kJ/mol, ≥about 18 kJ/mol, ≥about 20 kJ/mol, ≥about 22 kJ/mol, ≥about 24 kJ/mol, ≥about 26 kJ/mol, ≥about 28 kJ/mol, ≥about 30 kJ/mol, ≥about 32 kJ/mol, ≥about 34 kJ/mol, ≥about 36 kJ/mol, ≥about 38 kJ/mol or ≥about 40 kJ/mol. Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≤about 15 kJ/mol, ≤about 16 kJ/mol, ≤about 18 kJ/mol, ≤about 20 kJ/mol, ≤about 22 kJ/mol, ≤about 24 kJ/mol, ≤about 26 kJ/mol, ≤about 28 kJ/mol, ≤about 30 kJ/mol,

≤about 32 kJ/mol, ≤about 34 kJ/mol, ≤about 36 kJ/mol, ≤about 38 kJ/mol or ≤about 40 kJ/mol. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 15 kJ/mol to about 40 kJ/mol, about 18 kJ/mol to about 38 kJ/mol, about 20 kJ/mol to about 36 kJ/mol, about 22 kJ/mol to about 34 kJ/mol, etc. In particular, the adsorbent material may have an average heat of adsorption of about 20 kJ/mol to about 36 kJ/mol or about 22 kJ/mol to about 34 kJ/mol.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, DAC, EMT, EUO, IMF, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of CAS, EMT, FAU, HEU, IRR, IRY, ITT, LTA, RWY, TSC and VFI, and a combination thereof, having: (a) a Si/Al ratio of about 5 to about 85; and/or (b) a potassium cation concentration of about 5% to about 100%, for use in a PSA process for separating CO_2 from a feed gas mixture is provided.

In various aspects, an adsorbent material comprising a zeolite having a Si/Al ratio of between about 5 and about 45 and with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof, for use in a PSA process for separating CO_2 from a feed gas mixture is provided.

Nonlimiting examples of suitable zeolites for use in the PSA described herein are those which are provided below in Table 6.

TABLE 6

Zeolites
AFT_Si
AFX_Si
CAS_25_83
CAS_50_17
CHA_Si
DAC_Si
EMT_Si
EMT_50_100
EUO_Si
FAU_Si
FAU_50_67
FER_Si
HEU_50_100
IMF_Si
IRR_10_100
IRR_50_100
IRY_10_100
IRY_50_100
ITH_Si
ITT_Si
ITT_10_100
KFI_Si
LAU_Si
LTA_Si
LTA_50_67
MFI_Si
MFS_Si
MRE_Si
MTT_Si
MWW_Si
NES_Si
PAU_Si
RHO_Si
RRO_Si
RWY_5_100
RWY_10_100
SFF_Si
STF_Si
STI_Si
SZR_Si
TER_Si
TON_Si
TSC_Si
TSC_50_83
TUN_Si
UFI_Si
VFI_Si
VFI_10_100

B. Pressure Temperature Swing Adsorption (PTSA) Processes

In another embodiment, a PTSA process for separating CO_2 from a feed gas mixture is provided. The PTSA process may include subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed. The feed gas mixture may be natural gas, syngas, flue gas as well as other streams containing CO_2. Typical natural gas mixtures contain CH_4 and higher hydrocarbons (C_2H_6, C_3H_8, C_4H_{10} etc), as well as acid gases (CO_2 and H_2S), N_2 and H_2O. The amount of water in the natural gas mixture depends on prior dehydration processing to remove H_2O. Typical syngas mixtures contain H_2, CO, CO_2, CH_4, COS and H_2S. Typical flue gas mixtures contain N_2, CO_2, H_2O, O_2, SO_2. The adsorbent bed may comprise a feed input end, a product output end and an adsorbent material selective for adsorbing CO_2. Additionally, the adsorbent bed may be operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed.

The first temperature may be ≥about –30° C., ≥about –25° C., ≥about –20° C., ≥about –15° C., ≥about –10° C., ≥about –5° C., ≥about 0° C., ≥about 5° C., ≥about 10° C., ≥about 15° C., ≥about 20° C., ≥about 25° C., ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., or ≥about 100° C. In particular, the first temperature may be ≥about 25° C. Additionally or alternatively, the first temperature may be ≤about –30° C., ≤about –25° C., ≤about –20° C., ≤about –15° C., ≤about –10° C., ≤about –5° C., ≤about 0° C., ≤about 5° C., ≤about 10° C., ≤about 15° C., ≤about 20° C., ≤about 25° C., ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., or ≤about 100° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about –30° C. to about 100° C., about 25° C. to about 95° C., about –20° C. to about 80° C., about 0° C. to about 50° C., about 10° C. to about 30° C. In particular, the first temperature is about –20° C. to about 80° C., about 0° C. to about 50° C. or about 10° C. to about 30° C.

The first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 may be ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 5 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, ≥about 10 bar, ≥about 12 bar, ≥about 15 bar, ≥about 16 bar, ≥about 18 bar, ≥about 20 bar, ≥about 22 bar, ≥about 24 bar, ≥about 25 bar, ≥about 26 bar, ≥about 28 bar, or ≥about 30 bar. In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≥about 5 bar or ≥about 25 bar. Additionally or alternatively, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 5 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, ≤about 10 bar, ≤about 12 bar, ≤about 15 bar, ≤about 16 bar, ≤about 18 bar, ≤about 20 bar, ≤about 22 bar, ≤about 24 bar, ≤about 25 bar, ≤about 26 bar, ≤about 28 bar, or ≤about 30 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 1 bar to about 30 bar, about 2 bar to about 28 bar, about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 15 bar to about 25 bar. In particular, a first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 3 bar to about 7 bar, about 15 bar to about 25 bar, or about 18 bar to about 22 bar.

In various aspects, the PTSA process may further include stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed and heating the adsorbent bed to a second temperature, which may be higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a first portion of CO_2. The second temperature may be ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., ≥about 100° C., ≥about 105° C., ≥about 110° C., ≥about 115° C., ≥about 120° C., ≥about 125° C., ≥about 130° C., ≥about 135° C., ≥about 140° C., ≥about 145° C., ≥about 150° C., ≥about 155° C., ≥about 160° C., ≥about 165° C., ≥about 170° C., ≥about 175° C., ≥about 180° C., ≥about 185° C., ≥about 190° C., ≥about 195° C., or ≥about 200° C. In particular, the second temperature may be ≥about 95° C. Additionally or alternatively, the second temperature may be ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., ≤about 100° C., ≤about 105° C., ≤about 110° C., ≤about 115° C., ≤about 120° C., ≤about 125° C., ≤about 130° C., ≤about 135° C., ≤about 140° C., ≤about 145° C., ≤about 150° C., ≤about 155° C., ≤about 160° C., ≤about 165° C., ≤about 170° C., ≤about 175° C., ≤about 180° C., ≤about 185° C., ≤about 190° C., ≤about 195° C., or ≤about 200° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 30° C. to about 200° C., about 50° C. to about 150° C., about 55° C. to about 125° C., about 75° C. to about 120° C., about 80° C. to about 110° C., etc. In particular, the second temperature is about 50° C. to about 150° C., about 75° C. to about 120° C. or about 80° C. to about 110° C.

Additionally or alternatively, the PTSA process may further include reducing the pressure of the adsorbent bed to a second pressure, which may be lower than the first pressure, and recovering a second portion of CO_2. The second pressure in combination with above described second temperature may be such that the partial pressure of CO_2 is ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, or ≥about 10 bar. In particular, the second pressure in combination with above described second temperature may be such that the partial pressure of CO_2 is ≥about 1 bar. Additionally or alternatively, the second pressure in combination with above described second temperature may be such that the partial pressure of CO_2 is ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, or ≤about 10 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.1 bar to about 10 bar, about 0.3 bar to about 9 bar, about 0.5 bar to about 5 bar, about 0.5 bar to about 2 bar, about 1 bar to about 5 bar, etc. In particular, the second pressure in combination with above described second temperature may be such that the partial pressure of CO_2 is about 0.5 bar to about 2 bar, about 1 bar to about 5 bar, or about 0.9 bar to about 3 bar.

In various aspects, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, EMT, EUO, FAU, IRR, IRY, ITT, KFI, LTA, MRE, MWW, NES, PAU, RHO, RWY, SFF, STI, TSC, UFI, VFI, having (i) a Si/Al ratio of about 3 to about 100, about 3 to 75, about 5 to about 90, about 5 to about 85, about 5 to about 70, about 5 to about 60 or about 5 to about 50; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 100%, about 1% to about 100%, about 5% to about 100%, about 10% to about 100%, about 40% to about 100%, about 60% to about 100% or about 70% to about 100%.

Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, KFI, LTA, PAU, RHO, TSC, UFI, and a combination thereof, having (i) a Si/Al ratio of about 5 to about 60 or about 10 to about 50; and/or a (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 1% to about 100%, about 30% to about 100%, or about 50% to about 100%.

Additionally or alternatively, the above mentioned adsorbent materials may not include a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO and a combination thereof.

Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio of between about 5 and about 45 (e.g., about 6, about 10, about 20, about 30, about 40, etc.) and with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof. Additionally or alternatively, the adsorbent material may comprise a zeolite having a Si/Al ratio of between about 5 and about 45 (e.g., about 6, about 10, about 20, about 30, about 40, etc.) and with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may have a working capacity of ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Additionally or alternatively, the adsorbent material may have a working capacity of ≤about 1.0 mmol/cc, ≤about 2.0 mmol/cc, ≤about 3.0 mmol/cc, ≤about 4.0 mmol/cc, ≤about 5.0 mmol/cc, ≤about 6.0 mmol/cc, ≤about 7.0 mmol/cc, ≤about 8.0 mmol/cc, ≤about 9.0 mmol/cc, ≤about 10.0 mmol/cc, ≤about 11.0 mmol/cc, ≤about 12.0 mmol/cc, ≤about 13.0 mmol/cc, ≤about 14.0 mmol/cc, ≤about 15.0 mmol/cc, ≤about 16.0 mmol/cc, ≤about 17.0 mmol/cc,

≤about 18.0 mmol/cc, ≤about 19.0 mmol/cc, or ≤about 20.0 mmol/cc. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 1.0 mmol/cc to about 20.0 mmol/cc, about 1.0 mmol/cc to about 16.0 mmol/cc, about 2.0 mmol/cc to about 15.0 mmol/cc, about 3.0 mmol/cc to about 12.0 mmol/cc, about 3.0 mmol/cc to about 17.0 mmol/cc, about 5.0 mmol/cc to about 15.0 mmol/cc, etc. In particular, the adsorbent material may have a working capacity of about 3.0 mmol/cc to about 17.0 mmol/cc or about 5.0 mmol/cc to about 15.0 mmol/cc.

Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≥about 15 kJ/mol, ≥about 16 kJ/mol, ≥about 18 kJ/mol, ≥about 20 kJ/mol, ≥about 22 kJ/mol, ≥about 24 kJ/mol, ≥about 25 kJ/mol, ≥about 26 kJ/mol, ≥about 28 kJ/mol, ≥about 30 kJ/mol, ≥about 32 kJ/mol, ≥about 34 kJ/mol, ≥about 35 kJ/mol, ≥about 36 kJ/mol, ≥about 38 kJ/mol or ≥about 40 kJ/mol. Additionally or alternatively, the adsorbent may have an average heat of adsorption of ≤about 15 kJ/mol, ≤about 16 kJ/mol, ≤about 18 kJ/mol, ≤about 20 kJ/mol, ≤about 22 kJ/mol, ≤about 24 kJ/mol, ≤about 25 kJ/mol, ≤about 26 kJ/mol, ≤about 28 kJ/mol, ≤about 30 kJ/mol, ≤about 32 kJ/mol, ≤about 34 kJ/mol, ≤about 35 kJ/mol, ≤about 36 kJ/mol, ≤about 38 kJ/mol or ≤about 40 kJ/mol. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 15 kJ/mol to about 40 kJ/mol, about 18 kJ/mol to about 38 kJ/mol, about 20 kJ/mol to about 36 kJ/mol, about 22 kJ/mol to about 36 kJ/mol, about 24 kJ/mol to about 36 kJ/mol, about 25 kJ/mol to about 35 kJ/mol etc. In particular, the adsorbent material may have an average heat of adsorption of about 20 kJ/mol to about 38 kJ/mol, about 22 kJ/mol to about 36 kJ/mol or about 24 kJ/mol to about 36 kJ/mol.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, EMT, EUO, FAU, IRR, IRY, ITT, KFI, LTA, MRE, MWW, NES, PAU, RHO, RWY, SFF, STI, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 3 to about 100; and/or (b) a potassium cation concentration of about 1% to about 100%, for use in a PTSA process for separating CO_2 from a feed gas mixture is provided.

Nonlimiting examples of suitable zeolites for use in the PTSA described herein are those which are provided below in Table 7.

TABLE 7

Zeolites	
AFT_Si	MFI_Si
AFT_50_33	MFS_Si
AFX_Si	MRE_10_100
AFX_50_0	MTT_Si
CAS_Si	MWW_25_100
CHA_Si	MWW_50_100
CHA_25_50	NES_50_100
DAC_Si	PAU_Si
EMT_5_33	PAU_50_67
EMT_10_100	RHO_Si
EUO_25_100	RHO_25_83
FAU_5_83	RRO_Si
FER_Si	RWY_3_17
HEU_Si	SFF_Si
IMF_Si	SFF_50_100
IRR_5_50	STF_Si
IRR_10_33	STI_10_100
IRY_3_0	SZR_Si
IRY_10_67	TER_Si
ITH_Si	TON_Si
ITT_5_50	TSC_10_17
ITT_25_50	TSC_25_33
KFI_Si	TUN_Si
KFI_25_100	UFI_Si
LAU_Si	UFI_25_100
LTA_10_33	VFI_1_0
LTA_50_83	

C. Vacuum Swing Adsorption (VSA) Processes

In another embodiment, a VSA process for separating CO_2 from a feed gas mixture is provided. The VSA process may include subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed. The feed gas mixture may be natural gas, syngas, flue gas as well as other streams containing CO_2. Typical natural gas mixtures contain CH_4 and higher hydrocarbons (C_2H_6, C_3H_8, C_4H_{10} etc), as well as acid gases (CO_2 and H_2S), N_2 and H_2O. The amount of water in the natural gas mixture depends on prior dehydration processing to remove H_2O. Typical syngas mixtures contain H_2, CO, CO_2, CH_4, COS and H_2S. Typical flue gas mixtures contain N_2, CO_2, H_2O, O_2, SO_2. The adsorbent bed may comprise a feed input end, a product output end and an adsorbent material selective for adsorbing CO_2. Additionally, the adsorbent bed may be operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed.

The first temperature may be ≥about −30° C., ≥about −25° C., ≥about −20° C., ≥about −15° C., ≥about −10° C., ≥about −5° C., ≥about 0° C., ≥about 5° C., ≥about 10° C., ≥about 15° C., ≥about 20° C., ≥about 25° C., ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., or ≥about 100° C. In particular, the first temperature may be ≥about 25° C. Additionally or alternatively, the first temperature may be ≤about −30° C., ≤about −25° C., ≤about −20° C., ≤about −15° C., ≤about −10° C., ≤about −5° C., ≤about 0° C., ≤about 5° C., ≤about 10° C., ≤about 15° C., ≤about 20° C., ≤about 25° C., ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., or ≤about 100° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about −30° C. to about 100° C., about −25° C. to about 95° C., about −20° C. to about 80° C., about 0° C. to about 50° C., about 10° C. to about 30° C. In particular, the first temperature is about −20° C. to about 80° C., about 0° C. to about 50° C. or about 10° C. to about 30° C.

The first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 may be ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, or ≥about 10 bar.

In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≥about 1 bar. Additionally or alternatively, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, or ≤about 10 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.1 bar to about 10 bar, about 0.3 bar to about 9 bar, about 0.5 bar to about 5 bar, about 0.5 bar to about 3 bar, about 1 bar to about 5 bar, etc. In particular, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is about 0.5 bar to about 3 bar, about 0.5 bar to about 2 bar, about 1 bar to about 5 bar, or about 0.7 bar to about 2 bar.

In various aspects, the VSA process may further include stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed, passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure and in desorption of at least a portion of CO_2 from the adsorbent bed, and recovering at least a portion of CO_2 from the adsorbent bed. The second pressure may be such that the partial pressure of CO_2 is ≥about 0.01 bar, ≥about 0.02 bar, ≥about 0.03 bar, ≥about 0.04 bar, ≥about 0.05 bar, ≥about 0.06 bar, ≥about 0.07 bar, ≥about 0.08 bar, ≥about 0.09 bar, ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 0.95 bar or about 0.99 bar. In particular, the second pressure may be such that the partial pressure of CO_2 is ≥about 0.1 bar. Additionally or alternatively, the second pressure may be such that the partial pressure of CO_2 is ≤about 0.01 bar, ≤about 0.02 bar, ≤about 0.03 bar, ≤about 0.04 bar, ≤about 0.05 bar, ≤about 0.06 bar, ≤about 0.07 bar, ≤about 0.08 bar, ≤about 0.09 bar, ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 0.95 bar or ≤0.99 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.01 bar to about 0.99 bar, about 0.05 bar to about 0.8 bar, about 0.05 bar to about 0.5 bar, about 0.07 bar to about 0.4 bar, about 0.09 bar to about 0.2 bar, etc. In particular, the second pressure may be such that the partial pressure of CO_2 is about 0.05 bar to about 0.5 bar or about 0.09 bar to about 0.2 bar.

In various aspects, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a framework structure selected from the group consisting of CAS, DAC, HEU, LAU, MTT, RRO, TON, and a combination thereof. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, EMT, EUO, IMF, IRR, IRY, ITH, ITT, KFI, MFS, MRE, MWW, NES, PAU, RWY, SFF, STF, STI, SZR, TER, TSC, TUN, VFI, and a combination thereof, having (i) a Si/Al ratio of about 1 to about 100, about 1 to about 90, about 1 to about 75, about 1 to about 60 or about 1 to about 50; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 100%, about 5% to about 100%, about 10% to about 100%, about 10% to about 90%, about 40% to about 100%, about 60% to about 100% or about 70% to about 100%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFX, AFT, KFI, PAU, TSC, and a combination thereof, having (i) a Si/Al ratio of about 3 to about 60 or about 5 to about 50; and/or a (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 100%, about 10% to about 100%, about 30% to about 100%, about 50% to about 100%, or about 70% to about 100%.

Additionally or alternatively, the above mentioned adsorbent materials may not include a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO and a combination thereof.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof, having (i) a Si/Al ratio of between about 3 and about 50, about 4 to about 40, about 4 to about 30 or about 5 to about 25; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 20% to about 100%, about 30% to about 100%, about 40% to about 100%, about 50% to about 100%, or about 70% to about 100%. Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO, and a combination thereof, having (i) a Si/Al ratio of between about 3 and about 50, about 4 to about 40, about 4 to about 30 or about 5 to about 25; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 20% to about 100%, about 30% to about 100%, about 40% to about 100%, about 50% to about 100%, or about 70% to about 100%.

Additionally or alternatively, the adsorbent material may have a working capacity of ≥about 0.5 mmol/cc ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Additionally or alternatively, the adsorbent material may have a working capacity of ≤about 0.5 mmol/cc, ≤about 1.0 mmol/cc, ≤about 2.0 mmol/cc, ≤about 3.0 mmol/cc, ≤about 4.0 mmol/cc, ≤about 5.0 mmol/cc, ≤about 6.0 mmol/cc, ≤about 7.0 mmol/cc, ≤about 8.0 mmol/cc, ≤about 9.0 mmol/cc, ≤about 10.0 mmol/cc, ≤about 11.0 mmol/cc, ≤about 12.0 mmol/cc, ≤about 13.0 mmol/cc, ≤about 14.0 mmol/cc, ≤about 15.0 mmol/cc, ≤about 16.0 mmol/cc, ≤about 17.0 mmol/cc, ≤about 18.0 mmol/cc, ≤about 19.0 mmol/cc, or ≤about 20.0 mmol/cc. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 0.5 mmol/cc to about 20.0 mmol/cc, about 1.0 mmol/cc to about 16.0 mmol/cc, about 2.0 mmol/cc to about 15.0 mmol/cc, about 3.0 mmol/cc to about 12.0 mmol/cc, about 3.0 mmol/cc to about 10.0 mmol/cc, about 3.0 mmol/cc to about 6.0 mmol/cc etc. In particular, the adsorbent material may have a working capacity of about 3.0 mmol/cc to about 10.0 mmol/cc or about 3.0 mmol/cc to about 6.0 mmol/cc.

Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≥about 15 kJ/mol, ≥about 16 kJ/mol, ≥about 18 kJ/mol, ≥about 20 kJ/mol, ≥about 22 kJ/mol, ≥about 24 kJ/mol, ≥about 26 kJ/mol, ≥about 28 kJ/mol, ≥about 30 kJ/mol, ≥about 32 kJ/mol, ≥about 34 kJ/mol, ≥about 36 kJ/mol, ≥about 38 kJ/mol or ≥about 40 kJ/mol. Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≤about 15 kJ/mol, ≤about 16 kJ/mol, ≤about 18 kJ/mol, ≤about 20 kJ/mol, ≤about 22 kJ/mol, ≤about 24 kJ/mol, ≤about 26 kJ/mol, ≤about 28 kJ/mol, ≤about 30 kJ/mol, ≤about 32 kJ/mol, ≤about 34 kJ/mol, ≤about 36 kJ/mol, ≤about 38 kJ/mol or ≤about 40 kJ/mol. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 15 kJ/mol to about 40 kJ/mol, about 20 kJ/mol to about 38 kJ/mol, about 22 kJ/mol to about 38 kJ/mol, about 24 kJ/mol to about 38 kJ/mol etc. In particular, the adsorbent material for use in the PSA process described herein may have an average heat of adsorption of about 20 kJ/mol to about 38 kJ/mol or about 24 kJ/mol to about 38 kJ/mol.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of CAS, DAC, HEU, LAU, MTT, RRO, TON, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, EMT, EUO, IMF IRR, IRY, ITH, ITT, KFI, MFS, MRE, MWW, NES, PAU, RWY, SFF, STF, STI, SZR, TER, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100; and/or (b) a potassium cation concentration of about 0% to about 100%, for use in a VSA process for separating CO_2 from a feed gas mixture is provided.

In various aspects, an adsorbent material comprising a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI and a combination thereof, having (a) a Si/Al ratio of about 3 to about 30; and/or a potassium cation concentration of about 40% to about 100%, for use in a VSA process for separating CO_2 from a feed gas mixture is provided.

Nonlimiting examples of suitable zeolites for use in the VSA described herein are those which are provided below in Table 8.

TABLE 8

Zeolites	
RWY_3_17	HEU_Si
IRY_3_83	MWW_10_100
FAU_5_100	SFF_25_67
UFI_25_100	CAS_Si
KFI_25_100	TER_50_100
IRR_3_100	STI_10_83
EMT_5_83	MFS_25_100
RHO_10_50	TUN_50_100
AFX_25_33	NES_10_67
PAU_50_33	FER_50_100
VFI_1_0	ITH_25_100
AFT_25_83	LAU_Si
RRO_Si	MFI_50_100
CHA_25_83	SZR_50_83
DAC_Si	EUO_25_100
LTA_5_50	IMF_50_100
TSC_5_0	TON_Si
ITT_3_50	MTT_Si
STF_50_100	MRE_10_100

D. Vacuum Temperature Swing Adsorption (VTSA) Processes

In another embodiment, a VTSA process for separating CO_2 from a feed gas mixture is provided. The VTSA process may include subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed. The feed gas mixture may be natural gas, syngas, flue gas as well as other streams containing CO_2. Typical natural gas mixtures contain CH_4 and higher hydrocarbons (C2H6, C3H8, C4H10 etc), as well as acid gases (CO_2 and H_2S), N_2 and H_2O. The amount of water in the natural gas mixture depends on prior dehydration processing to remove H_2O. Typical syngas mixtures contain H_2, CO, CO_2, CH_4, COS and H_2S. Typical flue gas mixtures contain N_2, CO_2, H_2O, O_2, SO_2. The adsorbent bed may comprise a feed input end, a product output end and an adsorbent material selective for adsorbing CO_2. Additionally, the adsorbent bed may be operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed.

The first temperature may be ≥about −30° C., ≥about −25° C., ≥about −20° C., ≥about −15° C., ≥about −10° C., ≥about −5° C., ≥about 0° C., ≥about 5° C., ≥about 10° C., ≥about 15° C., ≥about 20° C., ≥about 25° C., ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., or ≥about 100° C. In particular, the first temperature may be ≥about 25° C. Additionally or alternatively, the first temperature may be ≤about −30° C., ≤about −25° C., ≤about −20° C., ≤about −15° C., ≤about −10° C., ≤about −5° C., ≤about 0° C., ≤about 5° C., ≤about 10° C., ≤about 15° C., ≤about 20° C., ≤about 25° C., ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., or ≤about 100° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about −30° C. to about 100° C., about −25° C. to about 95° C., about −20° C. to about 80° C., about 0° C. to about 50° C., about 10° C. to about 30° C. In particular, the first temperature is about −20° C. to about 80° C., about 0° C. to about 50° C. or about 10° C. to about 30° C.

The first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 may be ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, or ≥about 10 bar. In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≥about 1 bar. Additionally or alternatively, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar,

≤about 0.8 bar, ≤about 0.9 bar, ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, or ≤about 10 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.1 bar to about 10 bar, about 0.3 bar to about 9 bar, about 0.5 bar to about 7 bar, about 0.5 bar to about 6 bar, about 1 bar to about 5 bar, etc. In particular, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is about 0.5 bar to about 7 bar, about 0.5 bar to about 6 bar, about 1 bar to about 5 bar, or about 0.7 bar to about 2 bar.

In various aspects, the VTSA process may further include stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed and heating the adsorbent bed to a second temperature higher than the first temperature and passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2. The adsorbent bed may be heated simultaneously with passing the purge gas through though adsorbent bed. The second temperature may be ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., ≥about 100° C., ≥about 105° C., ≥about 110° C., ≥about 115° C., ≥about 120° C., ≥about 125° C., ≥about 130° C., ≥about 135° C., ≥about 140° C., ≥about 145° C., ≥about 150° C., ≥about 155° C., ≥about 160° C., ≥about 165° C., ≥about 170° C., ≥about 175° C., ≥about 180° C., ≥about 185° C., ≥about 190° C., ≥about 195° C., ≥about 200° C., ≥about 205° C., ≥about 210° C., ≥about 215° C., ≥about 220° C., ≥about 225° C., ≥about 250° C., ≥about 275° C., or ≥300° C. In particular, the second temperature may be ≥about 95° C. or ≥about 195° C. Additionally or alternatively, the second temperature may be ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., ≤about 100° C., ≤about 105° C., ≤about 110° C., ≤about 115° C., ≤about 120° C., ≤about 125° C., ≤about 130° C., ≤about 135° C., ≤about 140° C., ≤about 145° C., ≤about 150° C., ≤about 155° C., ≤about 160° C., ≤about 165° C., ≤about 170° C., ≤about 175° C., ≤about 180° C., ≤about 185° C., ≤about 190° C., ≤about 195° C., ≤about 200° C., ≤about 205° C., ≤about 210° C., ≤about 215° C., ≤about 220° C., ≤about 225° C., ≤about 250° C., ≤about 275° C., or ≤300° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 30° C. to about 300° C., about 50° C. to about 250° C., about 60° C. to about 200° C., about 75° C. to about 125° C., about 150° C. to about 250° C., bout 175° C. to about 225° C., etc. In particular, the second temperature is about 50° C. to about 250° C., about 75° C. to about 125° C. or about 175° C. to about 225° C.

The second pressure in combination with above described second temperature may be such that the partial pressure of CO_2 is ≥about 0.01 bar, ≥about 0.02 bar, ≥about 0.03 bar, ≥about 0.04 bar, ≥about 0.05 bar, ≥about 0.06 bar, ≥about 0.07 bar, ≥about 0.08 bar, ≥about 0.09 bar, ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 0.95 bar or about 0.99 bar. In particular, the second pressure may be such that the partial pressure of CO_2 is ≥about 0.1 bar or ≥about 0.2 bar. Additionally or alternatively, the second pressure may be such that the partial pressure of CO_2 is ≤about 0.01 bar, ≤about 0.02 bar, ≤about 0.03 bar, ≤about 0.04 bar, ≤about 0.05 bar, ≤about 0.06 bar, ≤about 0.07 bar, ≤about 0.08 bar, ≤about 0.09 bar, ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 0.95 bar or ≤0.99 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.01 bar to about 0.99 bar, about 0.05 bar to about 0.8 bar, about 0.05 bar to about 0.5 bar, about 0.07 bar to about 0.4 bar, about 0.09 bar to about 0.4 bar, about 0.08 bar to about 0.3 bar, etc. In particular, the second pressure may be such that the partial pressure of CO_2 is about 0.05 bar to about 0.5 bar, about 0.09 bar to about 0.4 bar or about 0.08 bar to about 0.3 bar.

In various aspects, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a CAS framework structure. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, EMT, EUO, HEU, IMF, IRR, IRY, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof, having (i) a Si/Al ratio of about 1 to about 100, about 1 to 90, about 1 to about 75, about 1 to about 50, about 1 to about 25, or about 1 to about 10; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 100%, about 0% to about 90%, about 0% to about 50%, about 0% to about 40%, or about 0% to about 30%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof, having (i) a Si/Al ratio of about 1 to about 30, about 1 to about 20, or about 1 to about 10; and/or a (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 50%, about 0% to about 40%, or about 0% to about 20%.

Additionally or alternatively, the above mentioned adsorbent materials may not include a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO and a combination thereof.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, MFI, RHO, UFI, and a combination thereof, having (i) a Si/Al ratio of between about 1 and about 30, about 1 to about 20, or about 1 to about 10; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 0% to about 20%, about 0% to about 10%, or about 0% to about 5%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a LTA framework structure having (i) a Si/Al ratio of between about 1 and about 20, about 1 to about 10, or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 2% to about 40%, about 5% to about 40%, about 5% to about 20%, or about 5% to about 10%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, RHO, and a combination thereof, having (i) a Si/Al ratio of between about 1 and about 30, about 1 to about 20, or about 1 to about 10; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 0% to about 20%, about 0% to about 10%, or about 0% to about 5%.

Additionally or alternatively, the adsorbent material may have a working capacity of ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Additionally or alternatively, the adsorbent material described herein may have a working capacity of ≤about 1.0 mmol/cc, ≤about 2.0 mmol/cc, ≤about 3.0 mmol/cc, ≤about 4.0 mmol/cc, ≤about 5.0 mmol/cc, ≤about 6.0 mmol/cc, ≤about 7.0 mmol/cc, ≤about 8.0 mmol/cc, ≤about 9.0 mmol/cc, ≤about 10.0 mmol/cc, ≤about 11.0 mmol/cc, ≤about 12.0 mmol/cc, ≤about 13.0 mmol/cc, ≤about 14.0 mmol/cc, ≤about 15.0 mmol/cc, ≤about 16.0 mmol/cc, ≤about 17.0 mmol/cc, ≤about 18.0 mmol/cc, ≤about 19.0 mmol/cc, or ≤about 20.0 mmol/cc. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 1.0 mmol/cc to about 20.0 mmol/cc, about 1.0 mmol/cc to about 16.0 mmol/cc, about 2.0 mmol/cc to about 15.0 mmol/cc, about 3.0 mmol/cc to about 14.0 mmol/cc, about 5.0 mmol/cc to about 12.0 mmol/cc, etc. In particular, the adsorbent material described herein may have a working capacity of about 3.0 mmol/cc to about 14.0 mmol/cc or about 5.0 mmol/cc to about 12.0 mmol/cc.

Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≥about 15 kJ/mol, ≥about 16 kJ/mol, ≥about 18 kJ/mol, ≥about 20 kJ/mol, ≥about 22 kJ/mol, ≥about 24 kJ/mol, ≥about 25 kJ/mol, ≥about 26 kJ/mol, ≥about 28 kJ/mol, ≥about 30 kJ/mol, ≥about 32 kJ/mol, ≥about 34 kJ/mol, ≥about 35 kJ/mol, ≥about 36 kJ/mol, ≥about 38 kJ/mol, ≥about 40 kJ/mol, ≥about 42 kJ/mol, ≥about 44 kJ/mol, ≥about 45 kJ/mol, ≥about 46 kJ/mol, ≥about 48 kJ/mol, ≥about 50 kJ/mol, ≥about 52 kJ/mol, ≥about 54 kJ/mol, ≥about 55 kJ/mol, ≥about 56 kJ/mol, ≥about 58 kJ/mol, or ≥about 60 kJ/mol. Additionally or alternatively, the adsorbent material may have an average heat of adsorption of ≤about 15 kJ/mol, ≤about 16 kJ/mol, ≤about 18 kJ/mol, ≤about 20 kJ/mol, ≤about 22 kJ/mol, ≤about 24 kJ/mol, ≤about 25 kJ/mol, ≤about 26 kJ/mol, ≤about 28 kJ/mol, ≤about 30 kJ/mol, ≤about 32 kJ/mol, ≤about 34 kJ/mol, ≤about 35 kJ/mol, ≤about 36 kJ/mol, ≤about 38 kJ/mol, ≤about 40 kJ/mol, ≤about 42 kJ/mol, ≤about 44 kJ/mol, ≤about 45 kJ/mol, ≤about 46 kJ/mol, ≤about 48 kJ/mol, ≤about 50 kJ/mol, ≤about 52 kJ/mol, ≤about 54 kJ/mol, ≤about 55 kJ/mol, ≤about 56 kJ/mol, ≤about 58 kJ/mol, or ≤about 60 kJ/mol. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 15 kJ/mol to about 60 kJ/mol, about 25 kJ/mol to about 58 kJ/mol, about 28 kJ/mol to about 54 kJ/mol, about 30 kJ/mol to about 55 kJ/mol, etc. In particular, the adsorbent material for use in the VTSA process described herein may have an average heat of adsorption of about 25 kJ/mol to about 58 kJ/mol, about 28 kJ/mol to about 54 kJ/mol or about 30 kJ/mol to about 55 kJ/mol.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 with a CAS framework structure; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, EMT, EUO, HEU, IMF, IRR, IRY, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100; and/or (b) a potassium cation concentration of about 0% to about 100%, for use in a VTSA process for separating CO_2 from a feed gas mixture is provided.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, MFI, RHO, UFI and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 5% to about 40%, for use in a VTSA process for separating CO_2 from a feed gas mixture is provided.

Nonlimiting examples of suitable zeolites for use in the VTSA described herein are those which are provided below in Table 9.

TABLE 9

Zeolites	
AFT_3_0	MFI_10_33
AFT_5_0	MFS_10_17
AFX_3_0	MRE_2_0
AFX_10_17	MTT_10_83
CAS_2_0	MWW_2_0
CAS_Si	MWW_2_33
CHA_10_0	NES_2_0
CHA_1_0	PAU_5_0
DAC_50_17	PAU_10_33
EMT_1_0	RHO_3_0
EMT_2_0	RHO_5_0
EUO_3_0	RRO_10_83
FAU_1_0	RWY_3_17
FAU_2_33	SFF_2_0
FER_10_33	SFF_3_0
HEU_25_17	STF_2_0
IMF_10_0	STF_5_0
IRR_2_0	STI_2_0
IRY_2_0	SZR_5_67
ITH_10_17	TER_10_17
ITT_2_0	TON_25_0
ITT_2_17	TSC_1_0
KFI_3_0	TUN_10_67
LAU_10_0	UFI_2_0
LTA_1_0	VFI_2_0
KFI_5_0	

E. Temperature Swing Adsorption (TSA) Processes

In another embodiment, a TSA process for separating CO_2 from a feed gas mixture is provided. The TSA process may include subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed. The feed gas mixture may be natural gas, syngas, flue gas as well as other streams containing CO_2. Typical natural gas mixtures contain CH_4 and higher hydrocarbons (C2H6, C3H8, C4H10 etc), as well as acid gases (CO_2 and H_2S), N_2 and H_2O. The amount of water in the natural gas mixture depends on prior dehydration processing to remove H_2O. Typical syngas mixtures contain H_2, CO, CO_2, CH_4, COS and H_2S. Typical flue gas mixtures contain N_2, CO_2, H_2O, O_2, SO_2. The adsorbent bed may comprise a feed input end, a product output end and an adsorbent material selective for adsorbing CO_2. Additionally, the adsorbent bed may be operated at a first pressure and at a first temperature wherein at least a portion of the

CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed.

The first temperature may be ≥about −30° C., ≥about −25° C., ≥about −20° C., ≥about −15° C., ≥about −10° C., ≥about −5° C., ≥about 0° C., ≥about 5° C., ≥about 10° C., ≥about 15° C., ≥about 20° C., ≥about 25° C., ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., or ≥about 100° C. In particular, the first temperature may be ≥about 25° C. Additionally or alternatively, the first temperature may be ≤about −30° C., ≤about −25° C., ≤about −20° C., ≤about −15° C., ≤about −10° C., ≤about −5° C., ≤about 0° C., ≤about 5° C., ≤about 10° C., ≤about 15° C., ≤about 20° C., ≤about 25° C., ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., or ≤about 100° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about −30° C. to about 100° C., about −25° C. to about 95° C., about −20° C. to about 80° C., about 0° C. to about 50° C., about 10° C. to about 30° C. In particular, the first temperature is about −20° C. to about 80° C., about 0° C. to about 50° C. or about 10° C. to about 30° C.

The first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 may be ≥about 0.1 bar, ≥about 0.2 bar, ≥about 0.3 bar, ≥about 0.4 bar, ≥about 0.5 bar, ≥about 0.6 bar, ≥about 0.7 bar, ≥about 0.8 bar, ≥about 0.9 bar, ≥about 1 bar, ≥about 2 bar, ≥about 3 bar, ≥about 4 bar, ≥about 6 bar, ≥about 7 bar, ≥about 8 bar, ≥about 9 bar, or ≥about 10 bar. In particular, the first pressure in combination with the above described first temperatures may be such that the partial pressure of CO_2 is ≥about 1 bar. Additionally or alternatively, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is ≤about 0.1 bar, ≤about 0.2 bar, ≤about 0.3 bar, ≤about 0.4 bar, ≤about 0.5 bar, ≤about 0.6 bar, ≤about 0.7 bar, ≤about 0.8 bar, ≤about 0.9 bar, ≤about 1 bar, ≤about 2 bar, ≤about 3 bar, ≤about 4 bar, ≤about 6 bar, ≤about 7 bar, ≤about 8 bar, ≤about 9 bar, or ≤about 10 bar. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 0.1 bar to about 10 bar, about 0.3 bar to about 9 bar, about 0.5 bar to about 5 bar, about 0.5 bar to about 3 bar, about 1 bar to about 5 bar, etc. In particular, the first pressure in combination with above described first temperature may be such that the partial pressure of CO_2 is about 0.5 bar to about 3 bar, about 0.5 bar to about 6 bar, about 1 bar to about 5 bar, or about 0.7 bar to about 2 bar.

In various aspects, the TSA process may further include stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed and heating the adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2 from the adsorbent bed. The second temperature may be ≥about 30° C., ≥about 35° C., ≥about 40° C., ≥about 45° C., ≥about 50° C., ≥about 55° C., ≥about 60° C., ≥about 65° C., ≥about 70° C., ≥about 75° C., ≥about 80° C., ≥about 85° C., ≥about 90° C., ≥about 95° C., ≥about 100° C., ≥about 105° C., ≥about 110° C., ≥about 115° C., ≥about 120° C., ≥about 125° C., ≥about 130° C., ≥about 135° C., ≥about 140° C., ≥about 145° C., ≥about 150° C., ≥about 155° C., ≥about 160° C., ≥about 165° C., ≥about 170° C., ≥about 175° C., ≥about 180° C., ≥about 185° C., ≥about 190° C., ≥about 195° C., ≥about 200° C., ≥about 205° C., ≥about 210° C., ≥about 215° C., ≥about 220° C., ≥about 225° C., ≥about 250° C., ≥about 275° C., or ≥300° C. In particular, the second temperature may be ≥about 95° C. or ≥about 195° C. Additionally or alternatively, the second temperature may be ≤about 30° C., ≤about 35° C., ≤about 40° C., ≤about 45° C., ≤about 50° C., ≤about 55° C., ≤about 60° C., ≤about 65° C., ≤about 70° C., ≤about 75° C., ≤about 80° C., ≤about 85° C., ≤about 90° C., ≤about 95° C., ≤about 100° C., ≤about 105° C., ≤about 110° C., ≤about 115° C., ≤about 120° C., ≤about 125° C., ≤about 130° C., ≤about 135° C., ≤about 140° C., ≤about 145° C., ≤about 150° C., ≤about 155° C., ≤about 160° C., ≤about 165° C., ≤about 170° C., ≤about 175° C., ≤about 180° C., ≤about 185° C., ≤about 190° C., ≤about 195° C., ≤about 200° C., ≤about 205° C., ≤about 210° C., ≤about 215° C., ≤about 220° C., ≤about 225° C., ≤about 250° C., ≤about 275° C., or ≤300° C. Ranges expressly disclosed include combinations of the above-enumerated upper and lower limits, e.g., about 30° C. to about 300° C., about 50° C. to about 250° C., about 60° C. to about 200° C., about 75° C. to about 125° C., about 150° C. to about 250° C., about 175° C. to about 225° C., etc. In particular, the second temperature is about 50° C. to about 250° C., about 150° C. to about 250° C., about 75° C. to about 125° C. or about 175° C. to about 225° C.

In various aspects, the adsorbent material may comprise a zeolite having a Si/Al ratio above about 100 (e.g. above about 200, above about 400, above about 600, etc.) and a CAS framework structure. Additionally or alternatively, these zeolites may include a cation concentration of less than about 10%, less than about 5%, less than about 1%, less than about 0.1%, or about 0%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, CAS, EMT, IRR, IRY, ITT, KFI, MWW, PAU, RWY, SFF, STF, TSC, UFI, VFI, and a combination thereof, having (i) a Si/Al ratio of about 1 to about 50, about 1 to 20, about 1 to about 10, or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 50%, about 0% to about 40%, about 0% to about 30%, or about 0% to about 20%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, UFI, and a combination thereof, having (i) a Si/Al ratio of about 1 to about 50, about 1 to 20, about 1 to about 10, or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 50%, about 0% to about 40%, about 0% to about 30%, or about 0% to about 20%.

Additionally or alternatively, the above mentioned adsorbent materials may not include a zeolite with a framework structure selected from the group consisting of CHA, FAU, LTA, RHO and a combination thereof.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, MFI, RHO, UFI, and a combination thereof, having (i) a Si/Al ratio of between about 1 and about 30, about 1 to about 20, about 1 to about 10 or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 0% to about 20%, about 0% to about 10%, or about 0% to about 5%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a LTA framework structure having (i) a Si/Al ratio of between about 1 and about 20, about 1 to about 10, or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 2% to about 40%, about 5% to about 40%, about 5% to about 20%, or about 5% to about 10%.

Additionally or alternatively, the adsorbent material may comprise a zeolite with a framework structure selected from the group consisting of CHA, FAU, RHO and a combination thereof, having (i) a Si/Al ratio of between about 1 and about 30, about 1 to about 20, about 1 to about 10 or about 1 to about 5; and/or (ii) a cation concentration (e.g., potassium cation, sodium cation) of about 0% to about 40%, about 0% to about 20%, about 0% to about 10%, or about 0% to about 5%.

Additionally or alternatively, the adsorbent material may have a working capacity of ≥about 1.0 mmol/cc, ≥about 2.0 mmol/cc, ≥about 3.0 mmol/cc, ≥about 4.0 mmol/cc, ≥about 5.0 mmol/cc, ≥about 6.0 mmol/cc, ≥about 7.0 mmol/cc, ≥about 8.0 mmol/cc, ≥about 9.0 mmol/cc, ≥about 10.0 mmol/cc, ≥about 11.0 mmol/cc, ≥about 12.0 mmol/cc, ≥about 13.0 mmol/cc, ≥about 14.0 mmol/cc, ≥about 15.0 mmol/cc, ≥about 16.0 mmol/cc, ≥about 17.0 mmol/cc, ≥about 18.0 mmol/cc, ≥about 19.0 mmol/cc, or ≥about 20.0 mmol/cc. Additionally or alternatively, the adsorbent material described herein may have a working capacity of ≤about 1.0 mmol/cc, ≤about 2.0 mmol/cc, ≤about 3.0 mmol/cc, ≤about 4.0 mmol/cc, ≤about 5.0 mmol/cc, ≤about 6.0 mmol/cc, ≤about 7.0 mmol/cc, ≤about 8.0 mmol/cc, ≤about 9.0 mmol/cc, ≤about 10.0 mmol/cc, ≤about 11.0 mmol/cc, ≤about 12.0 mmol/cc, ≤about 13.0 mmol/cc, ≤about 14.0 mmol/cc, ≤about 15.0 mmol/cc, ≤about 16.0 mmol/cc, ≤about 17.0 mmol/cc, ≤about 18.0 mmol/cc, ≤about 19.0 mmol/cc, or ≤about 20.0 mmol/cc. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 1.0 mmol/cc to about 20.0 mmol/cc, about 1.0 mmol/cc to about 16.0 mmol/cc, about 2.0 mmol/cc to about 15.0 mmol/cc, about 3.0 mmol/cc to about 14.0 mmol/cc, about 3.0 mmol/cc to about 12.0 mmol/cc, about 5.0 mmol/cc to about 10.0 mmol/cc, etc. In particular, the adsorbent material described herein may have a working capacity of about 3.0 mmol/cc to about 12.0 mmol/cc or about 5.0 mmol/cc to about 10.0 mmol/cc.

Additionally or alternatively, the adsorbent material for use in the TSA process described herein may have an average heat of adsorption of ≥about 15 kJ/mol, ≥about 16 kJ/mol, ≥about 18 kJ/mol, ≥about 20 kJ/mol, ≥about 22 kJ/mol, ≥about 24 kJ/mol, ≥about 25 kJ/mol, ≥about 26 kJ/mol, ≥about 28 kJ/mol, ≥about 30 kJ/mol, ≥about 32 kJ/mol, ≥about 34 kJ/mol, ≥about 35 kJ/mol, ≥about 36 kJ/mol, ≥about 38 kJ/mol, ≥about 40 kJ/mol, ≥about 42 kJ/mol, ≥about 44 kJ/mol, ≥about 45 kJ/mol, ≥about 46 kJ/mol, ≥about 48 kJ/mol, ≥about 50 kJ/mol, ≥about 52 kJ/mol, ≥about 54 kJ/mol, ≥about 55 kJ/mol, ≥about 56 kJ/mol, ≥about 58 kJ/mol, or ≥about 60 kJ/mol. Additionally or alternatively, the adsorbent material for use in the TSA process described herein may have an average heat of adsorption of ≤about 15 kJ/mol, ≤about 16 kJ/mol, ≤about 18 kJ/mol, ≤about 20 kJ/mol, ≤about 22 kJ/mol, ≤about 24 kJ/mol, ≤about 25 kJ/mol, ≤about 26 kJ/mol, ≤about 28 kJ/mol, ≤about 30 kJ/mol, ≤about 32 kJ/mol, ≤about 34 kJ/mol, ≤about 35 kJ/mol, ≤about 36 kJ/mol, ≤about 38 kJ/mol, ≤about 40 kJ/mol, ≤about 42 kJ/mol, ≤about 44 kJ/mol, ≤about 45 kJ/mol, ≤about 46 kJ/mol, ≤about 48 kJ/mol, ≤about 50 kJ/mol, ≤about 52 kJ/mol, ≤about 54 kJ/mol, ≤about 55 kJ/mol, ≤about 56 kJ/mol, ≤about 58 kJ/mol, or ≤about 60 kJ/mol. Ranges expressly disclosed include combinations of the above-enumerated values, e.g., about 15 kJ/mol to about 60 kJ/mol, about 25 kJ/mol to about 58 kJ/mol, about 28 kJ/mol to about 54 kJ/mol, about 28 kJ/mol to about 52 kJ/mol, etc. In particular, the adsorbent material for use in the TSA process described herein may have an average heat of adsorption of about 25 kJ/mol to about 58 kJ/mol, about 28 kJ/mol to about 54 kJ/mol or about 28 kJ/mol to about 52 kJ/mol.

In various aspects, an adsorbent material comprising a zeolite with a framework structure selected from the group consisting of AFT AFX, CAS, EMT, IRR, IRY, ITT, KFI, MWW, PAU, RWY, SFF, STF, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 0% to about 50%, for use in a TSA process for separating CO_2 from a feed gas mixture is provided.

In various aspects, an adsorbent material comprising one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, RHO, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 5% to about 40%, for use in a TSA process for separating CO_2 from a feed gas mixture is provided.

Nonlimiting examples of suitable zeolites for use in the TSA described herein are those which are provided below in Table 10.

TABLE 10

Zeolites
IRY_2_0
IRR_2_0
FAU_1_0
EMT_1_0
ITT_2_0
RHO_5_0
KFI_3_0
RWY_3_17
PAU_5_33
TSC_1_0
CHA_1_0
UFI_2_0
LTA_1_0
AFX_3_0
AFT_3_0
SFF_2_0
STF_5_0
MWW_3_0
VFI_2_0
CAS_2_0

Adsorptive kinetic separation processes, apparatuses, and systems, as described above, are useful for development and production of hydrocarbons, such as gas and oil processing. Particularly, the provided processes, apparatuses, and systems can be useful for the rapid, large scale, efficient separation of a variety of target gases from gas mixtures.

The provided processes, apparatuses, and systems may be used to prepare natural gas products by removing contaminants. The provided processes, apparatuses, and systems can be useful for preparing gaseous feed streams for use in utilities, including separation applications such as dew point control, sweetening/detoxification, corrosion protection/control, dehydration, heating value, conditioning, and purification. Examples of utilities that utilize one or more separation applications can include generation of fuel gas, seal gas, non-potable water, blanket gas, instrument and control gas, refrigerant, inert gas, and hydrocarbon recovery. Exemplary "not to exceed" product (or "target") acid gas removal specifications can include: (a) 2 vol % CO_2, 4 ppm H_2S; (b) 50 ppm CO_2, 4 ppm H_2S; or (c) 1.5 vol % CO_2, 2 ppm H_2S.

The provided processes, apparatuses, and systems may be used to remove acid gas from hydrocarbon streams. Acid gas removal technology becomes increasingly important as remaining gas reserves exhibit higher concentrations of acid (sour) gas resources. Hydrocarbon feed streams can vary widely in amount of acid gas, such as from several parts per million to 90 vol %. Non-limiting examples of acid gas concentrations from exemplary gas reserves can include concentrations of at least: (a) 1 vol % H_2S, 5 vol % CO_2; (b) 1 vol % H_2S, 15 vol % CO_2; (c) 1 vol % H_2S, 60 vol % CO_2; (d) 15 vol % H_2S, 15 vol % CO_2; or (e) 15 vol % H_2S, 30 vol % CO_2.

One or more of the following may be utilized with the processes, apparatuses, and systems provided herein, to prepare a desirable product stream, while maintaining relatively high hydrocarbon recovery:

(a) using one or more kinetic swing adsorption processes, such as pressure swing adsorption (PSA), temperature swing adsorption (TSA), and vacuum swing adsorption (VSA), including combinations of these processes; each swing adsorption process may be utilized with rapid cycles, such as using one or more rapid cycle pressure swing adsorption (RC-PDS) units, with one or more rapid cycle temperature swing adsorption (RC-TSA) units; exemplary kinetic swing adsorption processes are described in U.S. Patent Application Publication Nos. 2008/0282892, 2008/0282887, 2008/0282886, 2008/0282885, and 2008/0282884, which are each herein incorporated by reference in its entirety;

(b) removing acid gas with RC-TSA using advanced cycles and purges as described in U.S. Provisional Application No. 61/447,858, filed 1 Mar. 2011, as well as the U.S. patent application Ser. No. 13/406,079, claiming priority thereto, which are together incorporated by reference herein in their entirety;

(c) using a mesopore filler to reduce the amount of trapped methane in the adsorbent and increase the overall hydrocarbon recovery, as described in U.S. Patent Application Publication Nos. 2008/0282892, 2008/0282885, and 2008/028286, each of which is herein incorporated by reference in its entirety;

(d) depressurizing one or more RC-TSA units in multiple steps to intermediate pressures so that the acid gas exhaust can be captured at a higher average pressure, thereby decreasing the compression required for acid gas injection; pressure levels for the intermediate depressurization steps may be matched to the interstage pressures of the acid gas compressor to optimize the overall compression system;

(e) using exhaust or recycle streams to minimize processing and hydrocarbon losses, such as using exhaust streams from one or more RC-TSA units as fuel gas instead of re-injecting or venting;

(f) using multiple adsorbent materials in a single bed to remove trace amounts of first contaminants, such as H_2S, before removal of a second contaminant, such as CO_2; such segmented beds may provide rigorous acid gas removal down to ppm levels with RC-TSA units with minimal purge flow rates;

(g) using feed compression before one or more RC-TSA units to achieve a desired product purity;

(h) contemporaneous removal of non-acid gas contaminants such as mercaptans, COS, and BTEX; selection processes and materials to accomplish the same;

(i) using structured adsorbents for gas-solid contactors to minimize pressure drop compared to conventional packed beds;

(j) selecting a cycle time and cycle steps based on adsorbent material kinetics; and

(k) using a process and apparatus that uses, among other equipment, two RC-TSA units in series, wherein the first RC-TSA unit cleans a feed stream down to a desired product purity and the second RC-TSA unit cleans the exhaust from the first unit to capture methane and maintain high hydrocarbon recovery; use of this series design may reduce the need for a mesopore filler.

The processes, apparatuses, and systems provided herein can be useful in large gas treating facilities, such as facilities that process more than five million standard cubic feet per day (MSCFD) of natural gas, for example more than 15 MSCFD, more than 25 MSCFD, more than 50 MSCFD, more than 100 MSCFD, more than 500 MSCFD, more than one billion standard cubic feet per day (BSCFD), or more than two BSCFD.

FURTHER EMBODIMENTS

The invention can additionally or alternatively include one or more of the following embodiments.

Embodiment 1

A pressure swing adsorption process for separating CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, DAC, EMT, EUO, IMF, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of CAS, EMT, FAU, HEU, IRR, IRY, ITT, LTA, RWY, TSC and VFI, and a combination thereof, having: (a) a Si/Al ratio of about 5 to about 85 or about 5 to about 70; and/or (b) a potassium cation concentration of about 5% to about 100% or about 10% to about 100%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 15 bar to about 25 bar) and at a first temperature (e.g., about −20° C. to about 80° C., about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) reducing the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 2 bar) resulting in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 2

The process of embodiment 1, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of LTA, TSC, and a combination thereof, having: (a) a Si/Al ratio of about 40 to about 60; and/or (b) a potassium cation concentration of about 50% to about 90%.

Embodiment 3

A pressure swing adsorption process for separating CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite having a Si/Al ratio of between about 5 and about 45 and with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI, and a combination thereof; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 15 bar to about 25 bar) and at a first temperature (e.g., about −20° C. to about 80° C., about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) reducing the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 2 bar) resulting in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 4

The process of any one of the previous embodiments, wherein the adsorbent material has a working capacity of about 2.0 mmol/cc to about 15.0 mmol/cc.

Embodiment 5

A pressure temperature swing adsorption process for separating a CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, EMT, EUO, FAU, IRR, IRY, ITT, KFI, LTA, MRE, MWW, NES, PAU, RHO, RWY, SFF, STI, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 3 to about 100 or about 3 to about 75; and (b) a potassium cation concentration of about 1% to about 100%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 3 bar to about 25 bar, about 3 bar to about 10 bar, about 15 bar to about 25 bar) and at a first temperature (e.g., about −20° C. to about 80° C., from about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating the adsorbent bed to a second temperature (e.g., about 50° C. to about 150° C.) higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a first portion of CO_2; and d) reducing the pressure of the adsorbent bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 2 bar) lower than the first pressure and recovering a second portion of CO_2.

Embodiment 6

The process of embodiment 5, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, KFI, LTA, PAU, RHO, TSC, UFI and a combination thereof, having: (a) a Si/Al ratio of about 5 to about 60; and/or (b) a potassium cation concentration of about 1% to about 100%.

Embodiment 7

The process of embodiment 5 or 6, wherein the adsorbent material has a working capacity of about 3.0 mmol/cc to about 17.0 mmol/cc.

Embodiment 8

A vacuum swing adsorption process for separating CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following; (i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of CAS, DAC, HEU, LAU, MTT, RRO, TON, and a combination thereof; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, EMT, EUO, IMF, IRR, IRY, ITH, ITT, KFI, MFS, MRE, MWW, NES, PAU, RWY, SFF, STF, STI, SZR, TER, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100 or about 1 to about 75; and (b) a potassium cation concentration of about 0% to about 100%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 3 bar) and at a first temperature (e.g., about −20° C. to about 80° C.), wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.05 bar to about 0.5 bar) and in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 9

The process of embodiment 8, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of AFX, AFT, KFI, PAU, TSC, and a combination thereof, having: (a) a Si/Al ratio of about 3 to about 60; and (b) a potassium cation concentration of about 0% to about 100%.

Embodiment 10

A vacuum swing adsorption process for separating CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, LTA, MFI, RHO, UFI and a combination thereof, having (a) a Si/Al ratio of about 3 to about 30; and/or (b) a potassium cation concentration of about 40% to about 100%; wherein the adsorbent bed is operated at first pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 3 bar) and at a first temperature (e.g., about −20° C. to about 80° C.), wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.05 bar to about 0.5 bar) and in desorption of at least a portion of CO_2 from the adsorbent bed; and d) recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 11

The process of any one of embodiments 8-10, wherein the adsorbent material has a working capacity of about 3.0 mmol/cc to about 10.0 mmol/cc.

Embodiment 12

A vacuum temperature swing adsorption process for separating a CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite having a Si/Al ratio above about 100 with a CAS framework structure; or (ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, EMT, EUO, HEU, IRR, IRY, ITH, ITT, KFI, LAU, MFS, MRE, MTT, MWW, NES, PAU, RRO, RWY, SFF, STF, STI, SZR, TER, TON, TSC, TUN, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 100 or about 1 to about 75; and/or (b) a potassium cation concentration of about 0% to about 100% or about 0% to about 90%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 7 bar) and at a first temperature (e.g., about −20° C. to about 80° C., about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; and c) simultaneously heating the adsorbent bed to a second temperature (e.g., about 50° C. to about 250° C., about 75° C. to about 125° C., about 175° C. to about 225° C.) higher than the first temperature and passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.05 bar to about 0.5 bar, about 0.08 bar to about 0.3 bar, about 0.09 bar to about 0.4 bar), resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2.

Embodiment 13

The process of embodiment 12, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of AFX, AFT, KFI, PAU, TSC, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 0% to about 40%.

Embodiment 14

A vacuum temperature swing adsorption process for separating a CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, FER, MFI, RHO, UFI and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 5% to about 40%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 7 bar) and at a first temperature (e.g., about −20° C. to about 80° C., about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in

CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; and c) simultaneously heating the adsorbent bed to a second temperature (e.g., about 50° C. to about 250° C., about 75° C. to about 125° C., about 175° C. to about 225° C.) higher than the first temperature and passing a purge gas, substantially free of CO_2, through the adsorbent bed thereby resulting in a reduction in the pressure in the adsorption bed to a second pressure (e.g., such that the partial pressure of CO_2 is from about 0.05 bar to about 0.5 bar, about 0.08 bar to about 0.3 bar, about 0.09 bar to about 0.4 bar), resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2.

Embodiment 15

The process of any one of embodiments 12-14, wherein the adsorbent material has a working capacity of about 3.0 mmol/cc to about 14.0 mmol/cc.

Embodiment 16

A temperature swing adsorption process for separating CO_2 from a feed gas mixture (e.g., natural gas stream), wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of AFT AFX, CAS, EMT, IRR, IRY, ITT, KFI, MWW, PAU, RWY, SFF, STF, TSC, UFI, VFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20 or about 1 to about 10; and/or (b) a potassium cation concentration of about 0% to about 50% or about 0% to about 40%; wherein the adsorbent bed is operated at a first pressure (e.g., such that the partial pressure of CO_2 is from about 0.5 bar to about 3 bar, about 0.5 bar to about 3 bar) and at a first temperature (e.g., about −20° C. to about 80° C., about 0° C. to about 50° C.) wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating the adsorbent bed to a second temperature (e.g., about 150° C. to about 250° C.) higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 17

The process of embodiment 16, wherein the adsorbent material comprises a zeolite with a framework structure selected from the group consisting of AFX, AFT, KFI, PAU, TSC, UFI, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 10; and/or (b) a potassium cation concentration of about 0% to about 40%.

Embodiment 18

A temperature swing adsorption process for separating CO_2 from a feed gas mixture, wherein the process comprises: a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises: a feed input end and a product output end; and an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following: (i) a zeolite with a framework structure selected from the group consisting of CHA, FAU, RHO, and a combination thereof, having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 0% to about 40%; or (ii) a zeolite with a LTA framework structure having: (a) a Si/Al ratio of about 1 to about 20; and/or (b) a potassium cation concentration of about 5% to about 40%; the adsorbent bed is operated at a first pressure and at a first temperature wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed; b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed; c) heating adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a portion of CO_2 from the adsorbent bed.

Embodiment 19

The process of embodiments 16-18, wherein the adsorbent material has a working capacity of about 5.0 mmol/cc to about 12.0 mmol/cc.

Embodiment 20

The process of any one of the previous embodiments, wherein the adsorbent bed has open flow channels throughout its entire length through which the feed gas mixture is passed, e.g., a parallel channel contactor.

EXAMPLES

The following examples are merely illustrative, and do not limit this disclosure in any way.

Example 1—Gas Adsorption Simulation Studies

General Simulation Method

Roughly 220 zeolite topologies have been identified experimentally and are recognized by the International Zeolite Association (IZA) (Baerlocher, C.; McCusker, L. B., *Database of Zeolite Structures*. http://www.iza-structure.org/databases/, accessed on Apr. 14, 2015). In addition, large collections of hypothetical zeolite-like materials have been generated (Deem, M. W.; Pophale, R.; Cheeseman, P. A.; Earl, D. J. *J Phys Chem C* 2009, 113, 21353; Pophale, R.; Cheeseman, P. A.; Deem, M. W. *Phys Chem Phys* 2011, 13, 12407). An important simplification can be made by noting that only a fraction of the known experimental topologies (and none of the hypothetical materials) have known synthesis routes for aluminosilicate or siliceous materials. Most of the materials selected for calculations can be tested experimentally. First ten-membered ring (10MR) zeolites were considered. This choice avoids complications associated with the pore blocking and/or strongly hindered diffusion that can occur in K-containing zeolites with smaller pores. In the IZA database there are a total of 21 10MR topologies where aluminosilicate or silica analogues have been synthesized experimentally: DAC, EUO, FER, HEU, IMF, ITH, LAU, MFI, MFS, MRE, MTT, MWW, NES, RRO, SFF, STF, STI, SZR, TER, TON, TUN. In addition simulations were performed for 16 other topologies from the IZA database with large pore volumes (or void fraction), including three 18MR (IRR, VFI, ITT), one 16MR (IRY), three 12MR (FAU, EMT, RWY), and nine 8MR (LTA, TSC, AFT, AFX, CHA, KFI, PAU, RHO, UFI) zeolites. IRR, VFI, ITT, IRY, RWY, and AFT topologies were included because of their large pore volumes, although their siliceous or aluminosilicate analogues have not been synthesized experimentally to date.

For each topology, full optimizations of the siliceous structure were performed using the Hill-Sauer force field (Hill, J. R.; Sauer, J. *J Phys Chem* 1995, 99, 9536). Using these optimized frameworks, aluminosilicate structures were constructed with Si/Al ratios of 1, 2, 3, 5, 10, 25, and 50. Si atoms were randomly substituted by Al atoms obeying the Löwenstein's rule (Loewenstein, W. Am Mineral 1954, 39, 92). For the topologies that include odd numbered window sizes (e.g., 3, 5, and 7MR windows), it was therefore impossible to make structures with Si/Al=1, because Si and Al atoms cannot appear alternatively in these windows. For these topologies, the lowest Si/Al ratio used was 2 or 3. For each Si/Al ratio, K and/or Na extra-framework cations were introduced with the K/(K+Na) ratio chosen to be 0, 16.7, 33.4, 50, 66.7, 83.3, and 100%. For 10MR zeolites, this procedure generated 910 distinct materials.

The notation ZEO_A_B is used to represent cationic zeolites, where ZEO indicates the topology, A the Si/Al ratio, and B the percentage of potassium cations. Siliceous zeolites are denoted ZEO_Si. For instance, MFI_10_50 represents a zeolite material having the MFI topology, a Si/Al ratio of 10, and 50% K cations, while MFI_Si represents the siliceous MFI zeolite.

To get reliable cation distributions for each material, pre-equilibration simulations were performed prior to the adsorption of CO_2. In every material, Al atoms were randomly distributed subject to the Löwenstein rule (Loewenstein, W. Am Mineral 1954, 39, 92). Parallel tempering (also known as canonical replica-exchange Monte Carlo) was used in these simulations (Beauvais, C.; Guerrault, X.; Coudert, F. X.; Boutin, A.; Fuchs, A. H. *J Phys Chem B* 2004, 108, 399; Earl, D. J.; Deem, M. W. Phys Chem 2005, 7, 3910). For each cationic material, nine replicas were included in simulations at temperatures of 300, 390, 507, 659, 857, 1114, 1448, 1882, 2447 K, respectively. Adjacent temperatures are in a ratio of 1.3 for each temperature interval, as suggested in previous work (Beauvais, C.; Guerrault, X.; Coudert, F. X.; Boutin, A.; Fuchs, A. H. *J Phys Chem B* 2004, 108, 399). The lowest temperature was room temperature, and the highest temperature was high enough so as to ensure that no replicas become trapped in local energy minima. Reasonable degree of overlap between the potential energy distributions of neighboring state points was found.

Classical simulations were performed using the RASPA code developed by Dubbeldam and co-workers (Dubbeldam, D.; Calero, S.; Ellis, D. E.; Snurr, R. Q. Mol Simul 2015, 1; Dubbeldam, D.; Torres-Knoop, A.; Walton, K. S. Mol Simul 2013, 39, 1253), where the first-principles developed force fields as described above were used for calculating the interactions between CO_2 and zeolite as well as the interactions between cation and framework. Periodic boundary conditions were employed, vdW interactions were evaluated with the cutoff of 12 Å, and electrostatic energies were calculated using Ewald summation (Allen, M. P.; Tildesley, D. J. Computer Simulation of Liquids; Clarendon Press: Oxford, U. K., 1987; Frenkel, D.; Smit, B. Understanding Molecular Simulation: From Algorithms to Applications 2nd ed.; Academic Press: San Diego, Calif., 2002). Truncated potentials with tail corrections were used. During the simulations all framework atoms were fixed at their crystallographic positions while cations were allow to move.

Adsorption isotherms of CO_2 in zeolites were predicted computationally using standard Grand Canonical Monte Carlo (GCMC) methods, where volume (V), temperature (T), and chemical potential (μ) are held constant and the number of adsorbate molecules fluctuates. The chemical potential is determined from the fugacity, and the fugacity coefficients are computed using the Peng-Robinson equation of state (Robinson, D. B.; Peng, D. Y.; Chung, S. Y. K. Fluid Phase Equilibr 1985, 24, 25). Isosteric heats of adsorption, Qst, defined as the difference in the partial molar enthalpy of the adsorption between the gas phase and the adsorbed phase, were obtained during GCMC simulations using (Snurr, R. Q.; Bell, A. T.; Theodorou, D. N. *J Phys Chem* 1993, 97, 13742)

$$Q_{st} = RT - \frac{\langle NV\rangle - \langle N\rangle\langle V\rangle}{\langle N^2\rangle - \langle N\rangle^2}$$

where T is the temperature, R is the gas constant, < > denotes the ensemble average, N is the number of adsorbed molecules, and V is the sum of the interactions of all adsorbed molecules among themselves and with the zeolite. Isosteric heats of adsorption at the limit of zero loading, Q_{st}^0, were calculated using NVT ensemble, where N=1 (Burtch, N. C.; Jasuja, H.; Dubbeldam, D.; Walton, K. S. *J Am Chem Soc* 2013, 135, 7172).

The number of simulation cycles were tested to ensure that the predicted values of these adsorption properties were well converged (with deviation less than 5%). For cation pre-equilibration 100,000 cycles were used, while for CO_2 adsorption 25,000 cycles were used to guarantee equilibration and the following 25,000 cycles were used to sample the desired thermodynamics properties.

Some topologies, for example, FAU and LTA, include regions such as sodalite cages that are inaccessible for CO_2 molecules. These regions were blocked in simulations to avoid spurious adsorption of CO_2 in these regions.

For the structures with low Si/Al ratios, the blockage effect from K+ cations locating at 8MR windows may exist, and GCMC simulations cannot account it. So that was kept it in mind when these structures were chosen for CO_2 capture.

Void fractions of zeolite structures were computed from Widom particle insertion using Helium. The pore volume is the void fraction times the unit cell volume. Surface areas were computed using N_2 as the probe molecule. For the calculations of pore volumes and surface areas, the Clay Force Field (CLAYFF) was used for the atoms of the zeolite, force field parameters from the previous work were used for He—He interactions (Talu, O.; Myers, A. L. *Colloid Surface A* 2001, 187, 83), and the TraPPE was used for N_2-N_2 interactions (Potoff, J. J.; Siepmann, J. I. *Aiche J* 2001, 47, 1676). Lorentz-Berthelot mixing rules was applied for the cross species interactions (Cygan, R. T.; Liang, J.-J.; Kalinichev, A. G. *J Phys Chem B* 2004, 108, 1255).

Pore sizes including the largest cavity diameter (LCD) and the pore limiting diameter (PLD) were computed using Zeo++ (Willems, T. F.; Rycroft, C.; Kazi, M.; Meza, J. C.;

Haranczyk, M. Micropor Mesopor Mat 2012, 149, 134), where the radii of O, Si, and Al atoms in zeolite structures were adjusted to be 1.35 Å and the default CCDC radii were used for Na and K (2.27 and 2.75 Å, respectively).

In all simulations, framework atoms were fixed and extra-framework cations were allowed to move. Cation positions were determined using parallel tempering method prior to CO_2 adsorption. GCMC simulations were performed to predict the adsorbed amount of CO_2 and isosteric heat of adsorption at each condition in Table 1, while single-molecule NVT Monte Carlo simulations were used to compute the isosteric heat of adsorption at zero loading (Qst0) (Burtch, N. C.; Jasuja, H.; Dubbeldam, D.; Walton, K. S. J Am Chem Soc 2013, 135, 7172). Geometrical properties of the empty zeolite structures were calculated, including pore size in terms of pore limiting diameter (PLD), largest cavity diameter (LPD), accessible pore volume, and surface area.

To illustrate the approach, FIG. **1***a*-**1***d* shows the results for MWW zeolites topology. This figure shows that for each process the CO_2 working capacity varies with Si/Al ratio and cation composition, with the Si/Al ratio having a stronger influence on the working capacity.

For PSA the siliceous form of MMW has higher working capacity than the cationic analogues with high Si/Al ratios, which are in turn better than those with medium and low Si/Al ratios. Even though the adsorbed amounts of CO_2 in the cationic forms of MWW were larger than in the siliceous form at the adsorption condition, the cationic structures have lower working capacities due to the larger residual amounts of CO_2 at the desorption condition. The stronger CO_2 interactions created by the presence of extra-framework cations resulted in a trade-off between high total adsorption capacities and reduced working capacities.

In VSA (FIG. **1***b*), however, the cationic forms of MWW with Si/Al ratio around 25 perform better than those with lower and higher Si/Al ratios, including the siliceous analog of MWW. In PTSA and VTSA, the optimal Si/Al ratios lie at 50 and 10. The optimal MWW structures are determined to be MWW_Si, MWW_25_100, MWW_50_100, and MWW_10_17 for PSA, VSA, PTSA, and VTSA, respectively. The results in FIG. **1** represent a detailed, quantitative description of CO_2 adsorption in a wide range of MWW zeolites that would require enormously time-consuming synthesis and testing to establish experimentally. This kind of data, which we have calculated for all of the zeolite topologies listed above, greatly extends the number of zeolites for which thorough information is available regarding CO_2 adsorption. Using our results, we determined the optimal composition for each zeolite topology in each process, as characterized by CO_2 working capacity. Simulations were performed for process conditions listed in Table 4.

Example 1A—PSA1

Conditions:

Adsorption: 300K, 5 bar

Desorption: 300 K, 1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
RWY	3-10	0-100
IRY	3-25	0-100
FAU	25-inf	0-100
TSC	25-inf	0-100
IRR	3-25	0-100
EMT	25-inf	0-100
RHO	25-inf	0-100
UFI	25-inf	0-100
CHA	25-inf	0-100
AFT	25-inf	0-100
LTA	25-inf	0-100
AFX	25-inf	0-100
ITT	3-25	0-100
KFI	25-inf	0-100
VFI	3-25	0-100

The results are shown in Table 11

TABLE 11

PSA1 Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m3	Q_{st}^{ave} kJ/mol
RWY_5_100	6.49	10.90	4.41	26	27	38	12.69	6.45	0.67	867.28	27
IRY_10_100	4.98	8.42	3.44	26	25	44	10.55	6.71	0.58	1180.48	25
FAU_50_67	4.40	6.32	1.92	26	24	35	10.89	6.94	0.44	1292.53	25
TSC_50_83	4.36	6.68	2.32	26	27	38	15.19	3.89	0.46	1297.36	26
IRR_10_100	4.25	7.35	3.10	25	26	33	11.49	8.07	0.54	1173.74	25
EMT_50_100	4.12	6.08	1.96	26	24	36	11.30	6.94	0.44	1294.05	25
RHO_Si	4.02	7.01	2.99	27	26	29	10.62	3.82	0.46	1386.76	27
UFI_Si	4.01	6.85	2.84	30	26	28	10.33	3.41	0.44	1444.84	28
CHA_Si	3.86	6.60	2.74	30	26	22	7.23	3.82	0.42	1465.94	28
AFT_Si	3.77	6.78	3.02	30	27	28	7.59	3.67	0.42	1469.05	28
LTA_50_67	3.75	5.53	1.78	26	25	44	10.95	3.72	0.40	1362.60	26
AFX_Si	3.72	6.96	3.24	30	27	29	7.56	3.66	0.42	1468.58	28
ITT_10_100	3.60	7.07	3.47	25	27	38	11.58	8.02	0.49	1286.64	26
KFI_Si	3.58	7.47	3.89	31	31	29	10.74	4.06	0.42	1458.36	31
VFI_10_100	3.46	5.38	1.92	25	25	34	10.38	7.62	0.39	1457.56	25
SFF_Si	3.14	5.33	2.20	29	25	21	7.62	5.49	0.37	1605.67	27
STF_Si	3.13	6.02	2.89	33	27	22	7.67	5.52	0.38	1603.81	30
PAU_Si	3.00	7.20	4.20	32	31	30	10.55	3.82	0.38	1535.92	32
MWW_Si	2.91	4.72	1.81	25	23	22	9.76	4.94	0.40	1538.37	24
ITH_Si	2.50	4.64	2.14	28	26	23	6.74	4.74	0.32	1635.73	27
NES_Si	2.39	4.27	1.88	28	24	21	7.05	4.85	0.34	1600.43	26
TUN_Si	2.32	4.61	2.29	28	25	23	8.72	5.51	0.34	1628.85	26

TABLE 11-continued

PSA1 Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m3	Q_{st}^{ave} kJ/mol
TER_Si	2.24	4.75	2.51	28	26	23	6.98	5.17	0.34	1649.03	27
FER_Si	2.23	4.56	2.33	30	27	24	6.33	4.66	0.30	1704.70	29
MFS_Si	2.19	4.41	2.22	30	27	24	6.82	5.47	0.30	1685.27	28
IMF_Si	2.09	4.27	2.18	28	25	22	7.44	5.44	0.33	1648.76	26
STI_Si	2.08	4.37	2.29	28	25	23	6.04	5.01	0.35	1607.43	27
SZR_Si	1.95	4.19	2.24	31	28	20	6.26	4.62	0.28	1696.17	30
MFI_Si	1.92	4.36	2.44	28	26	24	6.85	5.55	0.32	1654.46	27
EUO_Si	1.88	3.73	1.85	28	25	23	7.10	4.88	0.32	1638.00	26
DAC_Si	1.81	6.53	4.72	34	32	33	5.34	3.85	0.31	1686.90	33
LAU_Si	1.81	4.43	2.62	30	28	24	6.04	4.10	0.30	1689.47	29
RRO_Si	1.59	5.83	4.24	34	33	29	4.67	4.19	0.29	1688.62	34
TON_Si	1.48	3.86	2.38	32	29	25	5.77	5.19	0.23	1759.92	31
MTT_Si	1.42	3.38	1.96	31	28	25	6.30	5.19	0.23	1760.11	29
CAS_50_17	1.33	4.45	3.12	35	35	35	4.97	2.93	0.16	1846.57	35
HEU_50_100	1.21	5.26	4.05	32	31	38	5.83	4.17	0.32	1666.11	32
MRE_Si	1.02	1.86	0.85	24	22	20	6.66	5.74	0.20	1779.94	23

Example 1B—PSA2

Conditions:
Adsorption: 300K, 20 bar
Desorption: 300 K, 1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
RWY	3-25	0-100
IRY	25-inf	0-100
IRR	25-inf	0-100
TSC	25-inf	0-100
ITT	25-inf	0-100
FAU	25-inf	0-100
EMT	25-inf	0-100
LTA	25-inf	0-100
RHO	25-inf	0-100
VFI	25-inf	0-100
UFI	25-inf	0-100
CHA	25-inf	0-100
AFT	25-inf	0-100
AFX	25-inf	0-100
KFI	25-inf	0-100

The results are shown in Table 12

TABLE 12

PSA2 Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
RWY_10_100	11.43	13.90	2.47	28	24	29	13.06	6.45	0.69	828.60	26
IRY_50_100	9.74	10.58	0.84	26	19	25	11.28	9.31	0.61	1129.92	23
IRR_50_100	8.92	9.90	0.98	25	20	24	14.84	9.21	0.57	1123.25	23
TSC_Si	7.96	9.46	1.49	29	26	28	16.07	3.89	0.47	1281.40	27
ITT_Si	7.64	8.58	0.94	24	20	21	13.84	12.34	0.53	1217.09	22
FAU_Si	7.31	8.39	1.09	29	20	18	10.89	6.94	0.45	1277.51	25
EMT_Si	7.17	8.26	1.09	29	20	19	11.30	6.95	0.45	1277.26	25
LTA_Si	6.70	7.55	0.86	29	21	19	10.95	3.72	0.42	1346.77	25
RHO_Si	6.50	9.49	2.99	30	26	29	10.62	3.82	0.46	1386.76	28
VFI_Si	6.25	6.55	0.30	24	15	13	12.29	11.61	0.42	1379.02	19
UFI_Si	5.97	8.80	2.84	31	26	28	10.33	3.41	0.44	1444.84	29
CHA_Si	5.89	8.63	2.74	31	26	22	7.23	3.82	0.42	1465.94	28
AFT_Si	5.79	8.80	3.02	31	27	28	7.59	3.67	0.42	1469.05	29
AFX_Si	5.56	8.80	3.24	32	27	29	7.56	3.66	0.42	1468.58	30
KFI_Si	5.28	9.17	3.89	30	31	29	10.74	4.06	0.42	1458.36	30
MWW_Si	4.95	6.76	1.81	28	23	22	9.76	4.94	0.40	1538.37	25
PAU_Si	4.66	8.86	4.20	31	31	30	10.55	3.82	0.38	1535.92	31
SFF_Si	4.60	6.80	2.20	30	25	21	7.62	5.49	0.37	1605.67	27
STF_Si	4.56	7.45	2.89	34	27	22	7.67	5.52	0.38	1603.81	31
CAS_25_83	1.88	4.20	2.32	33	34	39	4.97	2.93	0.15	1873.34	34

Example 1C—PTSA1

Conditions:
Adsorption: 300K, 5 bar
Desorption: 373 K, 1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
RWY	3-10	0-100
IRY	2-10	0-100
IRR	2-25	0-100
FAU	2-25	0-100
KFI	10-inf	0-100
RHO	10-inf	0-100
TSC	3-25	0-100
UFI	10-inf	0-100
EMT	2-25	0-100
ITT	2-25	0-100
PAU	25-inf	0-100
VFI	1-5	0-100
AFX	25-inf	0-100
AFT	25-inf	0-100
CHA	10-inf	0-100

The results are shown in Table 13

TABLE 13

PTSA1 Results											
Zeolite	ΔN mmol/ cc	N^{ads} mmol/ cc	N^{des} mmol/ cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
RWY_3_17	11.17	12.84	1.67	29	31	35	12.43	6.45	0.68	864.94	30
IRY_3_0	8.68	12.37	3.70	33	36	48	9.64	6.69	0.58	1216.97	35
IRR_5_50	7.76	9.56	1.80	28	33	43	12.01	7.98	0.54	1201.02	31
FAU_5_83	7.12	8.58	1.46	34	32	38	8.03	5.38	0.41	1402.97	33
KFI_25_100	6.99	8.22	1.23	33	33	36	10.74	4.06	0.40	1494.29	33
RHO_25_83	6.98	8.17	1.19	29	31	53	10.62	3.82	0.45	1418.05	30
TSC_10_17	6.87	8.11	1.25	28	34	46	13.46	3.89	0.45	1329.29	31
UFI_25_100	6.82	7.92	1.10	33	30	35	8.76	3.41	0.43	1480.44	32
EMT_5_33	6.74	8.74	2.00	33	33	44	9.60	6.79	0.43	1373.43	33
ITT_5_50	6.57	8.86	2.29	29	34	46	11.02	7.68	0.48	1318.02	32
PAU_50_67	6.40	7.77	1.37	33	32	39	9.61	3.82	0.37	1552.23	33
VFI_1_0	6.38	7.89	1.52	31	33	36	9.67	8.69	0.41	1630.18	32
AFX_50_0	6.36	7.57	1.22	32	31	37	7.56	3.66	0.41	1479.72	31
AFT_50_33	6.25	7.37	1.12	30	30	35	7.59	3.67	0.41	1482.92	30
CHA_25_50	6.24	7.52	1.28	32	31	36	7.23	3.82	0.41	1492.96	31
LTA_10_33	5.87	6.94	1.07	31	31	44	9.42	3.72	0.40	1401.43	31
STF_Si	5.50	6.02	0.52	33	23	22	7.67	5.52	0.38	1603.81	28
DAC_Si	5.42	6.53	1.11	34	31	33	5.34	3.85	0.31	1686.90	32
RRO_Si	5.06	5.83	0.77	34	30	29	4.67	4.19	0.29	1688.62	32
SFF_50_100	4.94	5.65	0.71	30	27	32	7.62	5.49	0.36	1625.45	29
MWW_25_100	4.90	5.83	0.93	29	29	36	9.76	4.77	0.37	1575.44	29
ITH_Si	4.22	4.64	0.42	28	24	23	6.74	4.74	0.32	1635.73	26
TER_Si	4.20	4.75	0.55	28	24	23	6.98	5.17	0.34	1649.03	26
STI_10_100	4.18	5.86	1.68	33	35	47	6.04	4.33	0.30	1698.98	34
NES_50_100	4.15	4.82	0.66	30	27	37	7.05	4.85	0.33	1620.85	29
CAS_Si	4.11	4.64	0.53	36	34	34	10.33	3.41	0.17	1833.03	35
TUN_Si	4.10	4.61	0.52	28	24	23	8.72	5.51	0.34	1628.85	26
HEU_Si	4.07	5.26	1.18	31	30	31	5.83	4.17	0.33	1646.28	31
FER_Si	4.05	4.56	0.51	30	25	24	6.33	4.66	0.30	1704.70	28
MFS_Si	3.97	4.41	0.44	30	24	24	6.82	5.47	0.30	1685.27	27
LAU_Si	3.81	4.43	0.63	30	26	24	6.04	4.10	0.30	1689.47	28
MFI_Si	3.79	4.36	0.56	28	25	24	6.85	5.55	0.32	1654.46	26
SZR_Si	3.78	4.19	0.41	31	25	20	6.26	4.62	0.28	1696.17	28
IMF_Si	3.78	4.27	0.49	28	23	22	7.44	5.44	0.33	1648.76	25
EUO_25_100	3.58	4.38	0.80	31	30	35	7.10	4.88	0.28	1677.21	30
TON_Si	3.32	3.86	0.54	32	26	25	5.77	5.19	0.23	1759.92	29
MTT_Si	2.89	3.38	0.49	31	26	25	6.30	5.19	0.23	1760.11	28
MRE_10_100	1.66	2.28	0.62	33	33	38	6.43	3.05	0.16	1881.31	33

Example 1D—PTSA2

Conditions:
Adsorption: 300K, 20 bar
Desorption: 373 K, 1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
RWY	3-10	0-100
IRY	2-25	0-100
IRR	2-25	0-100
TSC	10-inf	0-100
ITT	10-inf	0-100
RHO	25-inf	0-100
FAU	2-25	0-100
EMT	3-inf	0-100
KFI	25-inf	0-100
AFT	25-inf	0-100
UFI	25-inf	0-100
CHA	25-inf	0-100
AFX	25-inf	0-100
PAU	25-inf	0-100
VFI	1-5	0-100

The results are shown in Table 14

TABLE 14

PTSA2 Results

Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
RWY_3_17	14.39	16.06	1.67	32	31	35	12.43	6.45	0.68	864.94	32
IRY_10_67	11.21	12.13	0.92	30	28	42	10.82	7.23	0.59	1171.74	29
IRR_10_33	10.32	11.35	1.03	28	30	39	12.18	9.07	0.56	1155.96	29
TSC_25_33	9.31	9.93	0.62	29	30	40	14.97	3.89	0.46	1304.09	29
ITT_25_50	8.98	9.53	0.56	27	26	42	13.55	9.57	0.52	1239.83	27
RHO_Si	8.97	9.49	0.52	30	26	29	10.62	3.82	0.46	1386.76	28
FAU_5_83	8.65	10.11	1.46	34	32	38	8.03	5.38	0.41	1402.97	33
EMT_10_100	8.40	9.25	0.84	33	29	34	9.93	6.59	0.42	1350.71	31
KFI_Si	8.39	9.17	0.78	30	28	29	10.74	4.06	0.42	1458.36	29
AFT_Si	8.18	8.80	0.62	31	25	28	7.59	3.67	0.42	1469.05	28
UFI_Si	8.16	8.80	0.64	31	26	28	10.33	3.41	0.44	1444.84	29
CHA_Si	8.10	8.63	0.53	31	23	22	7.23	3.82	0.42	1465.94	27
AFX_Si	8.10	8.80	0.70	32	27	29	7.56	3.66	0.42	1468.58	30
PAU_Si	8.02	8.86	0.84	31	29	30	10.55	3.82	0.38	1535.92	30
VFI_1_0	7.67	9.19	1.52	31	33	36	9.67	8.69	0.41	1630.18	32
LTA_50_83	7.45	7.89	0.44	29	25	44	10.95	3.72	0.41	1362.60	27
STF_Si	6.93	7.45	0.52	34	23	22	7.67	5.52	0.38	1603.81	29
MWW_50_100	6.47	7.15	0.69	30	26	30	9.76	4.94	0.39	1558.59	28
SFF_Si	6.37	6.80	0.42	30	22	21	7.62	5.49	0.37	1605.67	26
CAS_Si	4.43	4.96	0.53	35	34	34	10.33	3.41	0.17	1833.03	35

Example 1E—VSA

Conditions:
Adsorption: 300K, 1 bar
Desorption: 300K, 0.1 bar

Optimal boundaries

Topology	Si/Al ratio	K/(K + Na)%
RWY	3-10	0-100
IRY	2-10	0-100
FAU	2-25	0-100
UFI	10-inf	0-100
KFI	10-inf	0-100
IRR	1-10	0-100

-continued

Optimal boundaries

Topology	Si/Al ratio	K/(K + Na)%
EMT	2-10	0-100
RHO	3-50	0-100
AFX	10-inf	0-100
PAU	25-inf	0-100
VFI	1-5	0-100
AFT	10-inf	0-100
RRO	25-inf	0-100
CHA	10-inf	0-100
DAC	25-inf	0-100

The results are shown in Table 15

TABLE 15

VSA Results

Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
RWY_3_17	5.34	7.33	1.99	30	34	35	12.43	6.45	0.68	864.94	32
IRY_3_83	4.48	7.54	3.06	30	35	47	10.18	5.45	0.54	1278.16	33
FAU_5_100	4.28	6.03	1.75	32	34	35	7.73	5.73	0.41	1411.84	33
UFI_25_100	3.98	5.20	1.22	32	32	35	8.76	3.41	0.43	1480.44	32
KFI_25_100	3.94	5.46	1.52	33	34	36	10.74	4.06	0.40	1494.29	33
IRR_3_100	3.79	6.47	2.68	31	37	43	12.81	7.31	0.50	1284.82	34
EMT_5_83	3.78	5.73	1.95	31	35	41	9.14	6.38	0.41	1401.81	33
RHO_10_50	3.59	6.66	3.06	32	36	56	8.94	3.82	0.43	1449.17	34
AFX_25_33	3.54	5.49	1.95	32	34	37	7.56	3.66	0.40	1494.57	33
PAU_50_33	3.53	5.26	1.73	33	33	50	10.01	3.82	0.37	1549.18	33
VFI_1_0	3.52	5.47	1.94	32	35	36	9.67	8.69	0.41	1630.18	34
AFT_25_83	3.51	4.94	1.43	31	32	42	7.59	3.67	0.40	1501.73	32
RRO_Si	3.43	4.24	0.80	33	31	29	4.67	4.19	0.29	1688.62	32
CHA_25_83	3.40	4.70	1.30	31	32	34	7.23	3.82	0.41	1497.78	32
DAC_Si	3.39	4.72	1.32	32	32	33	5.34	3.85	0.31	1686.90	32
LTA_5_50	3.30	5.54	2.24	33	36	46	8.17	3.71	0.39	1458.46	34
TSC_5_0	3.27	6.22	2.94	32	38	48	12.33	3.40	0.45	1359.20	35
ITT_3_50	3.16	7.06	3.90	31	39	53	10.45	7.76	0.46	1368.48	35
STF_50_100	3.13	3.94	0.81	30	30	33	7.67	5.52	0.36	1623.58	30
HEU_Si	2.84	4.14	1.30	31	32	31	5.83	4.17	0.33	1646.28	31

TABLE 15-continued

VSA Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
MWW_10_100	2.72	4.90	2.18	33	35	49	7.25	4.45	0.34	1625.99	34
SFF_25_67	2.69	4.01	1.32	30	33	51	7.62	5.49	0.35	1639.66	32
CAS_Si	2.61	3.37	0.76	35	35	34	10.33	3.41	0.17	1833.03	35
TER_50_100	2.31	3.16	0.86	28	30	33	6.98	5.17	0.32	1669.26	29
STI_10_83	2.29	4.46	2.17	34	36	47	6.04	4.22	0.31	1692.28	35
MFS_25_100	2.25	3.58	1.33	33	34	40	6.82	4.50	0.28	1725.88	33
TUN_50_100	2.23	2.94	0.71	27	29	31	8.72	5.51	0.32	1648.92	28
NES_10_67	2.22	4.56	2.34	35	37	51	7.04	4.02	0.30	1678.83	36
FER_50_100	2.18	2.96	0.78	30	31	35	6.33	4.65	0.29	1725.23	30
ITH_25_100	2.17	3.44	1.26	30	34	40	6.74	3.93	0.29	1675.66	32
LAU_Si	2.15	2.62	0.47	28	26	24	6.04	4.10	0.30	1689.47	27
MFI_50_100	2.13	2.97	0.84	28	30	43	6.85	5.55	0.31	1674.84	29
SZR_50_83	2.05	2.82	0.78	30	32	41	6.26	4.62	0.27	1715.03	31
EUO_25_100	1.98	2.83	0.84	29	32	35	7.10	4.88	0.28	1677.21	31
IMF_50_100	1.96	2.83	0.87	27	30	33	7.44	5.44	0.31	1668.62	29
TON_Si	1.95	2.38	0.43	29	27	25	5.77	5.19	0.23	1759.92	28
MTT_Si	1.59	1.96	0.37	28	26	25	6.30	5.19	0.23	1760.11	27
MRE_10_100	0.96	1.70	0.74	33	34	38	6.43	3.05	0.16	1881.31	34

Example 1F—VTSA1

Conditions:
Adsorption: 300K, 1 bar
Desorption: 373K, 0.1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
IRY	2-10	0-100
IRR	2-10	0-100
FAU	1-10	0-100
EMT	1-10	0-100
RWY	3-10	0-100
ITT	2-10	0-100

-continued

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
KFI	1-10	0-100
RHO	1-25	0-100
TSC	1-5	0-100
PAU	1-25	0-100
CHA	1-25	0-100
UFI	2-10	0-100
AFX	1-25	0-100
LTA	1-5	0-100
AFT	2-10	0-100

The results are shown in Table 16

TABLE 16

VTSA1 Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
IRY_2_0	8.78	10.07	1.29	32	42	48	11.00	6.80	0.58	1250.14	37
IRR_2_0	7.82	9.19	1.37	32	43	50	11.01	8.86	0.54	1244.85	38
FAU_2_33	7.51	8.17	0.66	37	40	44	7.77	4.29	0.42	1469.88	39
EMT_2_0	7.26	8.36	1.09	38	42	51	8.75	4.48	0.43	1432.34	40
RWY_3_17	7.14	7.33	0.20	30	31	35	12.43	6.45	0.68	864.94	31
ITT_2_17	6.92	8.33	1.41	33	45	54	10.78	7.88	0.48	1383.09	39
KFI_3_0	6.83	7.97	1.14	39	44	50	8.38	3.25	0.37	1591.16	41
RHO_5_0	6.71	8.39	1.68	36	46	58	9.03	3.82	0.44	1470.95	41
TSC_1_0	6.60	7.55	0.96	34	44	54	12.11	1.49	0.42	1514.78	39
PAU_10_33	6.41	7.39	0.98	36	44	54	8.55	3.82	0.35	1598.89	40
CHA_1_0	6.33	7.53	1.20	43	45	58	4.47	1.18	0.32	1732.93	44
UFI_2_0	6.14	7.65	1.52	35	45	49	7.86	2.25	0.42	1619.58	40
AFX_10_17	6.01	6.68	0.67	35	41	46	7.56	3.66	0.39	1523.45	38
LTA_1_0	5.93	7.42	1.49	38	46	48	7.60	1.49	0.38	1592.05	42
AFT_5_0	5.78	7.53	1.74	38	46	57	6.82	3.67	0.37	1558.23	42
VFI_2_0	5.31	5.68	0.38	32	38	45	9.70	8.26	0.40	1546.46	35
STF_5_0	5.24	6.84	1.59	41	45	53	6.13	3.05	0.34	1700.80	43
SFF_3_0	5.05	7.24	2.19	43	47	56	6.46	4.03	0.33	1751.88	45
MWW_2_33	4.87	6.70	1.83	40	46	61	7.35	1.87	0.31	1770.73	43
STI_2_0	4.82	7.18	2.36	45	49	56	4.92	2.86	0.30	1802.60	47
DAC_50_17	4.75	5.06	0.31	33	38	47	5.34	3.85	0.30	1700.19	36
RRO_10_83	4.57	5.22	0.64	38	44	54	4.66	2.98	0.23	1777.50	41
NES_2_0	4.47	7.03	2.56	45	49	59	5.57	3.10	0.30	1794.39	47
HEU_25_17	4.11	4.52	0.41	34	39	44	5.83	4.11	0.32	1672.23	36

TABLE 16-continued

VTSA1 Results											
Zeolite	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
MFS_10_17	4.04	4.90	0.86	36	44	54	6.82	3.68	0.28	1747.71	40
FER_10_33	3.79	4.52	0.74	35	43	51	6.32	3.25	0.27	1774.17	39
SZR_5_67	3.77	4.78	1.01	42	46	58	5.49	2.92	0.21	1849.39	44
EUO_3_0	3.77	5.67	1.91	38	48	57	6.00	3.26	0.28	1787.16	43
ITH_10_17	3.74	4.70	0.96	34	44	54	6.74	3.93	0.29	1696.30	39
TER_10_17	3.66	4.88	1.22	35	44	63	6.98	3.24	0.30	1709.97	39
TUN_10_67	3.60	4.09	0.48	33	39	46	6.99	3.52	0.29	1709.50	36
LAU_10_0	3.44	4.55	1.11	35	44	59	6.04	3.44	0.27	1745.57	40
MFI_10_33	3.34	4.23	0.88	34	43	57	6.85	3.02	0.29	1722.60	39
CAS_Si	3.31	3.37	0.06	35	34	34	10.33	3.41	0.17	1833.03	35
IMF_10_0	3.28	4.33	1.04	35	43	55	7.44	3.24	0.30	1702.98	39
MTT_10_83	2.60	2.93	0.33	35	40	43	6.29	2.92	0.19	1853.19	38
TON_25_0	2.46	2.91	0.46	32	42	53	5.77	5.19	0.22	1783.96	37
MRE_2_0	2.10	3.24	1.14	43	48	51	4.85	2.96	0.18	1996.05	45

Example 1G—VTSA2

Conditions:
Adsorption: 300K, 1 bar
Desorption: 473K, 0.2 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
IRY	2-10	0-100
FAU	1-10	0-100
EMT	1-10	0-100
IRR	2-5	0-100
ITT	2-10	0-100
RHO	1-10	0-100
PAU	2-10	0-100
KFI	1-10	0-100
UFI	1-5	0-100
TSC	1-10	0-100
CHA	1-10	0-100
AFT	1-10	0-100
AFX	1-10	0-100
RWY	3-10	0-100
LTA	1-10	0-100

The results are shown in Table 17

TABLE 17

VTSA2 Results											
Name	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
IRY_2_0	9.88	10.07	0.19	32	39	48	11.00	6.80	0.58	1250.14	36
FAU_1_0	9.28	9.62	0.34	40	45	52	7.60	3.01	0.41	1510.18	43
EMT_1_0	9.09	9.51	0.42	36	46	54	8.74	3.05	0.41	1509.89	41
IRR_2_0	8.97	9.19	0.22	32	41	50	11.01	8.86	0.54	1244.85	37
ITT_2_0	8.36	8.65	0.28	31	44	57	10.27	8.41	0.49	1364.86	38
RHO_3_0	8.19	8.53	0.34	36	49	58	7.73	2.44	0.42	1513.04	43
PAU_5_0	8.00	8.47	0.47	41	52	61	7.49	3.19	0.33	1629.16	47
KFI_3_0	7.80	7.97	0.16	39	41	50	8.38	3.25	0.37	1591.16	40
UFI_2_0	7.44	7.65	0.21	35	43	49	7.86	2.25	0.42	1619.58	39
TSC_1_0	7.42	7.55	0.13	34	40	54	12.11	1.49	0.42	1514.78	37
CHA_1_0	7.40	7.53	0.14	43	43	58	4.47	1.18	0.32	1732.93	43
AFT_3_0	7.37	7.73	0.36	39	47	56	5.67	3.67	0.36	1602.83	43
AFX_3_0	7.28	7.57	0.29	43	45	53	6.07	2.24	0.36	1602.31	44
RWY_3_17	7.28	7.33	0.06	30	28	35	12.43	6.45	0.68	864.94	29
LTA_1_0	7.22	7.42	0.20	38	42	48	7.60	1.49	0.38	1592.05	40
SFF_2_0	6.98	7.50	0.51	45	47	54	5.67	3.17	0.33	1800.62	46
MWW_2_0	6.82	7.41	0.59	40	50	58	7.71	2.40	0.35	1725.15	45
STF_2_0	6.62	7.14	0.52	44	48	55	5.56	3.07	0.33	1798.92	46
VFI_2_0	5.61	5.68	0.07	32	35	45	9.70	8.26	0.40	1546.46	33
CAS_2_0	3.97	4.23	0.25	43	60	67	3.86	1.96	0.14	2055.60	51

Example 1H—VTSA3

Conditions:
Adsorption: 300K, 5 bar
Desorption: 473K, 0.2 bar
The results are shown in Table 18

TABLE 18

VTSA3 Results	
Zeolite	ΔN mmol/cc
RWY_3_17	12.78
IRY_2_0	12.74
IRR_2_0	11.60
FAU_1_0	10.76
ITT_2_0	10.51
EMT_1_0	10.34
RHO_5_0	9.73
TSC_1_0	9.23
PAU_5_0	8.99
KFI_5_0	8.90
UFI_2_0	8.56
AFT_5_0	8.39
AFX_5_0	8.37
LTA_1_0	8.12
CHA_10_0	7.95
VFI_1_0	7.85
SFF_2_0	7.69
MWW_2_0	7.68
STF_5_0	7.43
CAS_Si	4.62

Example 1I—TSA

Conditions:
Adsorption: 300K, 1 bar
Desorption: 473K, 1 bar

Optimal boundaries		
Topology	Si/Al ratio	K/(K + Na)%
IRY	2-10	0-100
IRR	2-10	0-100
FAU	1-10	0-100
EMT	1-10	0-100
ITT	2-10	0-100
RHO	1-25	0-100
KFI	1-10	0-100
RWY	1-10	0-100
PAU	1-25	0-100
TSC	1-10	0-100
CHA	1-10	0-100
UFI	1-10	0-100
LTA	1-10	0-100
AFX	1-10	0-100
AFT	1-10	0-100

The results are shown in Table 19

TABLE 19

TSA Results											
Name	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	Q_{st}^{ads} kJ/mol	Q_{st}^{des} kJ/mol	Q_{st}^{0} kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	Q_{st}^{ave} kJ/mol
IRY_2_0	9.21	10.07	0.86	32	39	48	11.00	6.80	0.58	1250.14	36
IRR_2_0	8.26	9.19	0.94	32	40	50	11.01	8.86	0.54	1244.85	36
FAU_1_0	8.21	9.62	1.41	40	45	52	7.60	3.01	0.41	1510.18	43
EMT_1_0	7.93	9.51	1.59	36	45	54	8.74	3.05	0.41	1509.89	41
ITT_2_0	7.53	8.65	1.12	31	43	57	10.27	8.41	0.49	1364.86	37
RHO_5_0	7.34	8.39	1.05	36	44	58	9.03	3.82	0.44	1470.95	40
KFI_3_0	7.25	7.97	0.72	39	42	50	8.38	3.25	0.37	1591.16	41
RWY_3_17	7.07	7.33	0.27	30	28	35	12.43	6.45	0.68	864.94	29
PAU_5_33	6.97	8.13	1.16	40	47	57	7.07	3.19	0.32	1651.71	44
TSC_1_0	6.96	7.55	0.59	34	41	54	12.11	1.49	0.42	1514.78	37
CHA_1_0	6.84	7.53	0.69	43	43	58	4.47	1.18	0.32	1732.93	43
UFI_2_0	6.72	7.65	0.94	35	42	49	7.86	2.25	0.42	1619.58	39
LTA_1_0	6.52	7.42	0.91	38	41	48	7.60	1.49	0.38	1592.05	40
AFX_3_0	6.46	7.57	1.11	43	44	53	6.07	2.24	0.36	1602.31	43
AFT_3_0	6.42	7.73	1.31	39	46	56	5.67	3.67	0.36	1602.83	43
SFF_2_0	5.86	7.50	1.63	45	48	54	5.67	3.17	0.33	1800.62	46
STF_5_0	5.72	6.84	1.11	41	44	53	6.13	3.05	0.34	1700.80	43
MWW_3_0	5.62	7.32	1.70	38	47	60	7.52	2.80	0.36	1678.46	42
VFI_2_0	5.34	5.68	0.34	32	35	45	9.70	8.26	0.40	1546.46	33
CAS_2_0	3.37	4.23	0.85	43	57	67	3.86	1.96	0.14	2055.60	50

Example 1J—PSA3

Conditions:
Adsorption: 300K, 0.066 bar
Desorption: 300K, 0.0026 bar
The results are shown in Table 20

TABLE 20

PSA3 Results

Name	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	$Q_{st}{}^{ads}$ kJ/mol	$Q_{st}{}^{des}$ kJ/mol	$Q_{st}{}^{0}$ kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	$Q_{st}{}^{ave}$ kJ/mol
FAU_1_0	4.53	7.10	2.57	45	48	52	7.60	3.01	0.41	1510.18	47
KFI_1_0	4.48	6.21	1.73	49	50	52	6.98	1.22	0.34	1723.96	49
EMT_1_0	4.29	6.99	2.71	45	49	54	8.74	3.05	0.41	1509.89	47
CHA_1_0	4.26	5.54	1.28	47	47	58	4.47	1.18	0.32	1732.93	47
IRY_2_0	4.21	5.31	1.10	39	46	48	11.00	6.80	0.58	1250.14	42
IRR_2_0	4.11	5.41	1.31	41	47	50	11.01	8.86	0.54	1244.85	44
UFI_2_0	3.93	5.43	1.50	43	48	49	7.86	2.25	0.42	1619.58	45
LTA_1_0	3.92	5.44	1.51	44	49	48	7.60	1.49	0.38	1592.05	46
TSC_1_0	3.84	4.75	0.91	43	47	54	12.11	1.49	0.42	1514.78	45
RHO_3_0	3.74	5.88	2.15	41	49	58	7.73	2.44	0.42	1513.04	45
AFX_3_0	3.67	5.48	1.81	45	48	53	6.07	2.24	0.36	1602.31	46
AFT_3_0	3.61	5.98	2.37	45	49	56	5.67	3.67	0.36	1602.83	47
ITT_2_17	3.59	4.94	1.35	42	48	54	10.78	7.88	0.48	1383.09	45
PAU_5_33	3.49	5.67	2.18	44	50	57	7.07	3.19	0.32	1651.71	47
MWW_2_33	3.43	5.24	1.80	44	47	61	7.35	1.87	0.31	1770.73	46
SFF_2_0	3.17	5.99	2.82	48	50	54	5.67	3.17	0.33	1800.62	49
STF_2_0	2.87	5.44	2.57	46	49	55	5.56	3.07	0.33	1798.92	48
VFI_2_17	1.94	2.20	0.26	38	44	45	9.86	7.94	0.39	1566.89	41
CAS_2_0	1.50	3.68	2.18	52	56	67	3.86	1.96	0.14	2055.60	54
RWY_3_17	1.34	1.41	0.07	34	35	35	12.43	6.45	0.68	864.94	34

Example 1K—PSA4

Conditions:
Adsorption: 233K, 0.066 bar
Desorption: 233K, 0.0026 bar
The results are shown in Table 21

TABLE 21

PSA4 Results

Name	ΔN mmol/cc	N^{ads} mmol/cc	N^{des} mmol/cc	$Q_{st}{}^{ads}$ kJ/mol	$Q_{st}{}^{des}$ kJ/mol	$Q_{st}{}^{0}$ kJ/mol	LCD (Di) Å	PLD (Df) Å	Accessible volume-	density kg/m^3	$Q_{st}{}^{ave}$ kJ/mol
RWY_3_17	6.99	9.50	2.50	29	36	35	12.43	6.45	0.68	864.94	32
FAU_5_0	5.77	8.75	2.98	34	36	43	8.97	4.63	0.43	1355.07	35
UFI_25_100	5.74	7.10	1.36	31	34	35	8.76	3.41	0.43	1480.44	33
KFI_50_100	5.53	6.66	1.13	31	34	32	10.74	4.06	0.41	1476.32	32
PAU_Si	5.32	6.14	0.82	33	32	30	10.55	3.82	0.38	1535.92	32
AFX_25_100	5.00	6.78	1.78	32	34	36	7.56	3.66	0.39	1504.77	33
CHA_25_100	4.93	6.19	1.26	31	34	32	7.23	3.82	0.41	1500.19	32
EMT_5_67	4.92	7.55	2.64	31	35	44	8.96	6.59	0.42	1392.94	33
STF_50_100	4.86	5.65	0.79	31	33	33	7.67	5.52	0.36	1623.58	32
RHO_10_100	4.83	7.88	3.05	32	35	56	7.98	3.82	0.42	1466.50	34
AFT_25_0	4.81	6.80	1.99	31	35	55	7.59	3.67	0.41	1489.49	33
IRY_5_50	4.46	7.09	2.63	29	36	44	10.09	6.33	0.57	1208.08	33
IRR_5_50	4.43	7.05	2.62	29	36	43	12.01	7.98	0.54	1201.02	33
LTA_10_100	4.42	5.41	0.99	30	35	36	8.28	3.72	0.38	1422.00	32
VFI_1_0	4.25	6.84	2.58	32	37	36	9.67	8.69	0.41	1630.18	34
TSC_10_0	4.05	6.07	2.02	29	36	45	13.61	3.89	0.46	1323.95	33
ITT_5_100	3.71	6.14	2.43	29	35	44	11.20	7.01	0.46	1345.06	32
SFF_25_67	3.62	5.08	1.45	30	35	51	7.62	5.49	0.35	1639.66	33
MWW_10_100	3.49	6.01	2.52	33	35	49	7.25	4.45	0.34	1625.99	34
CAS_Si	3.44	4.48	1.04	36	36	34	10.33	3.41	0.17	1833.03	36

The relationship between the working capacity and accessible pore volume for the optimal composition of each topology has been investigated. Interestingly, almost linear correlations were observed for all these processes. FIG. **2** shows the case for PSA1. Based on the linear relationships, the upper bound of the working capacity for a specified process could be estimated for a zeolite material once its accessible pore volume was determined.

It was further found that their average Qst are located in a narrow range for each process. FIG. **3** shows the case for PSA1. The mean value with the standard deviation for all these optimal compositions were calculated to be 27±3, 32±2, 30±3, and 40±4 kJ/mol for PSA1, VSA, PTSA1, and VTSA1, respectively. In contrast, their heats of adsorption at zero coverage (Qst0) were located in a relatively larger range for each process (not shown). The results mean that suitable average Qst were required for maximizing the working capacity of each topology in a specified process. Too high an average Qst will lead to a large amount of residual adsorbed adsorbate at the desorption pressure, and therefore to a reduced working capacity, whereas too low an average Qst will also result in a low working capacity. As a result, for each topology there was an optimal average Qst for obtaining the maximum working capacity.

It was found that for each zeolite topology there was an optimal composition (Si/Al ratio and K/(K+Na) ratio) that yields the highest working capacity for the topology. Although for a specified process the optimal composition is topology-dependent, the average heats of adsorption of the optimal composition are close for different topologies. The highest performing materials were found to have both large pore volume and the optimal average heats of adsorption.

Example 2—Validation of Simulations

CO_2 adsorption isotherms simulated with the developed CCFF force field were compared with the experimental data for a range of zeolites with different Si/Al ratios and cation compositions. FIG. **4** shows the comparison for CO_2 in several pure K- and mixed cation zeolites. The calculated results come from our first-principles derived force fields; these calculations were not fitted to experimental data in any way. For K-CHA (Si/Al=12, FIGS. **4***a* and **4***b*), the simulated isotherms based on CCFF are in excellent agreement with the experimental data from Pham et al. at all three temperatures. For K-MCM-22 (Si/Al=15, FIGS. **4***c* and **4***d*), CCFF makes predictions that are in reasonable agreement with experimental data reported by Zukal et al. at room and high temperatures, but slightly underestimates the CO_2 loading at low pressures and overestimates at high pressures at 273 K. FIG. **4***e* shows the comparison for CO_2 adsorption in KX and KY. Both materials have the same topology, FAU, but with different Si/Al ratios, 1.23 for KX and 2.37 for KY. The experimental samples prepared by Walton et al. have the compositions K76Na10Al86Si106O384 and K5Na52Al57Si135O384 for KX (88.7% K) and KY (91.7% K), respectively (Walton, K. S.; Abney, M. B.; LeVan, M. D. Micropor Mesopor Mat 2006, 91, 78). Reasonable agreement was found between the simulated isotherms and the experiments for these two samples, although CCFF may overestimate CO_2 loading slightly at low pressures for KX. The higher adsorption capacity of KX compared to KY in the medium pressure region may be due to the higher concentration of cation sites in KX, especially dual cation sites, where one CO_2 molecule can effectively interact with two cations.

Finally, the force fields were applied to K/Na-LTA (Si/Al=1). Previous studies on separation of CO_2/N_2 using K/Na-LTA showed that K cations make it difficult for CO_2 to diffuse in the zeolite because they block 8MR windows. GCMC simulations alone cannot account for the blockage effect. Data was chosen from a sample with composition K17Na79Al96Si96O384 (17.4% K), since the blockage effect is likely to be small for this composition (Liu, Q. L.; Mace, A.; Bacsik, Z.; Sun, J. L.; Laaksonen, A.; Hedin, N. Chem Commun 2010, 46, 4502). As shown in FIG. **4***f*, the simulated isotherms at 29 8K and 343 K agree well with the experimental data reported by Liu et al. (Liu, Q. L.; Mace, A.; Bacsik, Z.; Sun, J. L.; Laaksonen, A.; Hedin, N. Chem Commun 2010, 46, 4502), but overestimated at 253 K for the whole pressure region. The significant deviation may be due to the slow adsorption kinetics of CO_2 in experimental measurement at this low temperature (Cheung, O.; Bacsik, Z.; Liu, Q. L.; Mace, A.; Hedin, N. Appl Energ 2013, 112, 1326).

The good performance of the CCFF force fields for CO_2 adsorption in the diverse zeolite samples represented in FIG. **4** indicates that this approach accurately describes these materials. This outcome means that for the first time a reliable force field for CO_2 adsorption in Na- and K-containing zeolites for the full range of Si/Al ratios is available. This situation opens the possibility of applying these methods to screening of zeolite materials for CO_2 capture at different process conditions.

CO_2 adsorption isotherms were determined for the following zeolites in order to validate the simulations. High-resolution adsorption isotherms of carbon dioxide were obtained by employing three different adsorption instruments. For measurements below 1 atm Autosorb-1 volumetric instrument (Quantachrome Instr.) and in-house Cahn gravimetric microbalance were used. For high-pressure measurements volumetric instrument iSORB (Quantachrome Instr.) was used. Prior to each adsorption experiment, zeolite samples were subjected to in-situ outgassing at 400 C under vacuum of the order of 1×10^{-4} torr. The experimental isotherms were converted from excess to absolute adsorption using the theoretical (helium) pore volumes according to (Neimark, A. V.; Ravikovitch, P. I. *Langmuir,* 1997, 13, 5148)

$$N_{abs}=N_{ex}+\rho V_p$$

SSZ-35 (STF Framework Structure)

A gel of composition: 10.2 SDAOH: 2.65 Na_2O: Al_2O_3: 124 SiO_2: 1714 H_2O was prepared by mixing 18.2 g of deionzed water, 7.5 g of Cab-O-Sil fumed silica, 13.8 g of 13.65% 6,10-dimethyl-5-azoniaspiro(4,5)decane hydroxide, 0.4 g 50% sodium hydroxide, 0.2 g $Al(OH)_3$ (53% Al_2O_3), and 20 mg of SSZ-35 seeds in a plastic beaker with a spatula. The mixture was thoroughly homogenized in a 125 ml blender for 20 minutes and then placed in a 45 ml teflon-lined autoclave. The autoclave was placed in 170° C. oven and tumbled at 43 rpm for 7 days. The product was vacuum filtered, washed with de-ionized water and dried in an air oven at 110° C. Phase analysis by powder X-ray diffraction showed the sample to be pure SSZ-35 zeolite. The sample was then calcined in air for three hours at 600° C. to remove the organic template.

The sample was then ammonium exchanged by mixing 6.3 g of the calcined sample with 6.3 g NH_4Cl in 63 mls de-ionized water for 1 hr at 60-80° C. on a hot plate stirrer. The sample was then calcined again at 600° C. for three hours in air, and then re-exchanged a second time as before. Elemental analysis by ICP gave Si/Al=78 and Na/Al=0.04.

The CO_2 adsorption isotherm for SSZ-35 is shown in FIG. **5**, which shows the comparison to the simulations (open squares) and the experimental SSZ-35 (points).

SSZ-13 (CHA Framework Structure)

A gel of composition: 3 SDAOH: 10 Na_2O: Al_2O_3: 35 SiO_2: 1000 H_2O was prepared by adding 8.9 g of 25% trimethyladamantaammonium hydroxide, 0.7 g of 50% NaOH, 21.0 g of sodium silicate (29% SiO_2, 9% Na2O), 42.3 g of de-ionized water and 2.1 g of USY zeolite (Englehard EZ-190, 60.2% SiO_2, 17.2% Al_2O_3) to a 125 ml teflon autoclave. The mixture was reacted for three days at 140° C. in a tumbling oven rotating at 20 rpm. The product was vacuum filtered, washed with de-ionized water and dried in an air oven at 115° C. Phase analysis by powder X-ray diffraction showed the sample to be pure SSZ-13 zeolite. Elemental analysis by ICP gave Si/Al=8.2 and Na/Al=0.49.

Zeolite RHO

A gel of composition: 0.44 Cs_2O: 0.5 TEA_2O: 2.46 Na_2O: Al_2O_3: 11.1 SiO_2: 110 H_2O was prepared by first preparing a cesium, sodium aluminate solution by dissolving 7.9 g

NaOH in 10 mls distilled H_2O and 10.4 g 50% CsOH. Added 6.16 g of $Al_2O_3.3H_2O$ and heated to a boil until alumina dissolved and then cooled down to room temperature. To a 250 ml beaker added 65.8 g of 40% colloidal silica (Ludox HS-40), 14.5 g of 40% TEAOH, cesium, sodium aluminate solution and enough water to bring the total weight of solution to 125 g. The solution was mixed thoroughly with a spatula, transferred to a 125 ml teflon bottle and allow to age at room temperature for four days and then in an 85° C. oven for three days. The product was vacuum filtered, washed with distilled water and dried in an air oven at 115° C. Phase analysis by powder X-ray diffraction showed the sample to be pure RHO zeolite. Elemental analysis by ICP and AA gave Si/Al=3.1, Cs/Al=0.45, and Na/Al=0.51.

In another example SSZ-13 material has been prepared with Si/Al=7, and Na/Al=0.75. CO_2 adsorption isothermss for SSZ-13 (open symbols) at different temperatures are compared to the simulated CO_2 adsorption isotehrms (solid symbols) in FIG. **6**.

SSZ-16 (AFX Framework Structure)

A gel of composition: 0.3 SDA(OH)2: 0.3 NaOH: 0.025 Al_2O_3: SiO_2: 30 H_2O was prepared by adding 15.7 g Ludox LS-30 colloidal silica, 31.6 g of 22.6% Pentane-1,5-bis(N-methylpiperidinium hydroxide), 1.5 g of 50% NaOH, 0.8 g USALCO 45 sodium aluminate solution (19.3% Na2O, 25% Al_2O_3), and 5.4 g deionized water to a plastic beaker. The mixture was stirred for three hours and then placed in two 23 and one 45 ml teflon autoclaves. It was then reacted for three days at 160° C. in a tumbling oven rotating at 20 rpm. The product was vacuum filtered, washed with de-ionized water and dried in an air oven at 115° C. Phase analysis by powder X-ray diffraction showed the sample to be pure SSZ-16 zeolite. Elemental analysis by ICP gave Si/Al=4.7 and Na/Al=0.59.

CO_2 adsorption isotherms for SSZ-16 (points) are compared to the simulated CO_2 adsorption (lines) in FIG. **7**.

What is claimed is:

1. A pressure temperature swing adsorption process for separating a CO_2 from a feed gas mixture, wherein the process comprises:

a) subjecting the feed gas mixture comprising CO_2 to an adsorption step by introducing the feed gas mixture into a feed input end of an adsorbent bed, wherein the adsorbent bed comprises:

a feed input end and a product output end; and

an adsorbent material selective for adsorbing CO_2, wherein the adsorbent material comprises one or more of the following:

(i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof; or

(ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, EMT, EUO, FAU, IRR, IRY, ITT, KFI, LTA, MRE, MWW, NES, PAU, RHO, RWY, SFF, STI, TSC, UFI, VFI, and a combination thereof, having:

a. a Si/Al ratio of about 3 to about 100; and

b. a potassium cation concentration of about 1% to about 100%;

wherein the adsorbent bed is operated at a first pressure and at a first temperature, and wherein at least a portion of the CO_2 in the feed gas mixture is adsorbed by the adsorbent bed and wherein a gaseous product depleted in CO_2 exits the product output end of the adsorbent bed;

b) stopping the introduction of the feed gas mixture to the adsorbent bed before breakthrough of CO_2 from the product output end of the adsorbent bed;

c) heating the adsorbent bed to a second temperature higher than the first temperature, resulting in desorption of at least a portion of CO_2 from the adsorbent bed and recovering at least a first portion of CO_2; and

d) reducing the pressure of the adsorbent bed to a second pressure lower than the first pressure and recovering a second portion of CO_2, and

wherein the first temperature is from about −20° C. to about 80° C. and the first pressure is such that the partial pressure of CO_2 is from about 3 bar to about 25 bar.

2. The process of claim **1**, wherein the first temperature is from about 0° C. to about 50° C. and the first pressure is such that the partial pressure of CO_2 is from about 3 bar to about 10 bar.

3. The process of claim **1**, wherein the first temperature is from about 0° C. to about 50° C. and the first pressure is such that the partial pressure of CO_2 is from about 15 bar to about 25 bar.

4. The process of claim **1**, wherein the second temperature is from about 50° C. to about 150° C., and the second pressure is such that the partial pressure of CO_2 is from about 0.5 bar to about 2 bar.

5. The process of claim **1**, wherein the feed gas mixture is a natural gas stream.

6. The process of claim **1**, wherein the adsorbent material has a working capacity of about 3.0 mmol/cc to about 17.0 mmol/cc.

7. The process of claim **1**, wherein the adsorbent bed has open flow channels throughout its entire length through which the feed gas mixture is passed.

8. The process of claim **7**, wherein the adsorbent bed is a parallel channel contactor.

9. The process of claim **1**, wherein the adsorbent material is a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, CAS, DAC, HEU, IMF, ITH, KFI, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof.

10. The process of claim **1**, wherein the adsorbent material is a zeolite with a framework structure selected from the group consisting of EUO, IRR, IRY, ITT, MRE, MWW, NES, PAU, RWY, SFF, STI, UFI, VFI, and a combination thereof, having:

a. a Si/Al ratio of about 3 to about 75; and

b. a potassium cation concentration about 1% to about 100%.

11. The process of claim **1**, wherein the adsorbent material comprises one or more of the following:

(i) a zeolite having a Si/Al ratio above about 100 and a framework structure selected from the group consisting of AFT, AFX, KFI, PAU, TSC, and a combination thereof; or

(ii) a zeolite with a framework structure selected from the group consisting of AFT, AFX, CHA, KFI, LTA, PAU, RHO, TSC, UFI and a combination thereof, having:

a. a Si/Al ratio of about 5 to about 60; and

b. a potassium cation concentration of about 1% to about 100%.

12. The process of claim **1**, wherein the adsorbent material is a zeolite having a Si/Al ratio above about 100 with a framework structure selected from the group consisting of

CAS, DAC, IMF, ITH, LAU, MFS, MTT, PAU, RRO, SFF, STF, SXR, TER, TON, TUN, and a combination thereof.

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